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最終頁に続く

(54)【発明の名称】　排気ガス浄化用触媒の製造方法、及び排気ガス浄化用触媒を用いた排気ガスフィルター及び排気ガス浄化装置並びに排気ガス浄化システム

(57)【要約】

【課題】　内燃機関の排気ガスに含まれる硫黄酸化物との反応を抑えて、硫黄酸化物に対する耐被毒性に優れた排気ガス浄化用触媒の製造方法、排気ガスフィルター、排気ガス浄化装置および排気ガス浄化システムを提供することを目的とする。

【解決手段】　本発明の排気ガス浄化用触媒の製造方法は、触媒活性成分を触媒担体上に含浸担持する担持工程において、触媒活性成分と担体を混合した混合溶液中に、分子の構成成分に硫黄を含む、触媒活性成分と錯体を形成する錯化剤を適量添加し、前記混合溶液を撹拌、乾燥後、還元雰囲気中、所定の温度で焼成し、更に酸化雰囲気中、所定の温度で焼成する。また、望ましくは更に、硫黄酸化物を含む酸化雰囲気中、所定の温度で焼成する構成を有する。

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【特許請求の範囲】

【請求項１】多孔性無機物からなる担体と、前記担体の表面上に担持された貴金属、卑金属、金属酸化物の内のいずれか一種類以上からなる触媒活性成分と、を有する排気ガス浄化用触媒の製造方法であって、前記担体に前記触媒活性成分を担持する担持工程を有し、前記担持工程で使用される前記触媒活性成分に前記触媒活性成分と錯体を形成する錯化剤が添加されていることを特徴とする排気ガス浄化用触媒の製造方法。

【請求項２】前記錯化剤が、前記触媒活性成分に配位する原子として硫黄を含有することを特徴とする請求項１に記載の排気ガス浄化用触媒の製造方法。

【請求項３】前記錯化剤がジエチルジチオカルバミン酸誘導体の塩であることを特徴とする請求項１又は２に記載の排気ガス浄化用触媒の製造方法。

【請求項４】前記ジエチルジチオカルバミン酸誘導体の塩がジエチルジチオカルバミン酸ジエチルアンモニウムであることを特徴とする請求項３に記載の排気ガス浄化用触媒の製造方法。

【請求項５】前記錯化剤の添加量ａが触媒活性成分の添加量ｂに対して、モル比（ａ／ｂ）が１～１０、好ましくは３～５に調整されていることを特徴とする請求項１乃至４に記載の排気ガス浄化用触媒の製造方法。

【請求項６】前記担持工程が前記触媒活性成分と前記担体と前記錯化剤の混合溶液のｐＨを０．１～２．０、好ましくは１．５～２に調整して行われることを特徴とする請求項１乃至５の内いずれか１に記載の排気ガス浄化用触媒の製造方法。

【請求項７】前記混合溶液のｐＨを調整するためのｐＨ調整剤として塩素を含有しない酸を用いることを特徴とする請求項６に記載の排気ガス浄化用触媒の製造方法。

【請求項８】前記触媒を担持した前記担体を焼成する焼成工程が、酸化雰囲気下で焼成する酸化焼成工程を有することを特徴とする請求項１乃至７の内いずれか１に記載の排気ガス浄化用触媒の製造方法。

【請求項９】前記酸化焼成工程が、酸化雰囲気中所定の温度で焼成を行った後に、更に硫黄酸化物ガスを含む酸化雰囲気下所定の温度で焼成を行うことを特徴とする請求項８に記載の排気ガス浄化用触媒の製造方法。

【請求項１０】前記酸化焼成工程が、酸化雰囲気中所定の温度で焼成を行った後に、更に硫黄酸化物ガス及び水蒸気を含む酸化雰囲気下で所定の温度で焼成を行うことを特徴とする請求項８又は９の内いずれか１に記載の排気ガス浄化用触媒の製造方法。

【請求項１１】前記酸化焼成工程の硫黄酸化物ガスの存在下又は硫黄酸化物ガス及び水蒸気を含む酸化雰囲気下での焼成温度が、１００～１０００℃、好ましくは４００～５００℃で行うことを特徴とする請求項８乃至１０の内いずれか１に記載の排気ガス浄化用触媒の製造方法。

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【請求項１２】前記酸化焼成工程の硫黄酸化物ガスの存在下又は硫黄酸化物ガス及び水蒸気を含む酸化雰囲気下での焼成時間が１～１００時間、好ましくは２０～３０時間であることを特徴とする請求項８乃至１１の内いずれか１に記載の排気ガス浄化用触媒の製造方法。

【請求項１３】前記担体がシリカをコーティングした活性アルミナであることを特徴とする請求項１乃至１２の内いずれか１に記載の排気ガス浄化用触媒の製造方法。

【請求項１４】前記活性アルミナの比表面積が５０～２００m^2／ｇ、中心粒子径が０．３～１０μｍ、細孔容積が０．４ｃｃ／ｇ～１ｃｃ／ｇを有することを特徴とする請求項１３記載の排気ガス浄化用触媒の製造方法。

【請求項１５】本体が円柱状又は角柱状に形成され軸方向に多数のセルを有し前記各セルの両端面のいずれか一方を封止剤で封止されたセラミック製のハニカム構造体と、前記ハニカム構造体のセル壁に担持された請求項１乃至１４の内いずれか１に記載の排気ガス浄化用触媒の製造方法で作製された排気ガス浄化用触媒と、を備えたことを特徴とする排気ガスフィルター。

【請求項１６】請求項１５に記載された排気ガスフィルターと、前記排気ガスフィルターを加熱する加熱手段と、を有することを特徴とする排気ガス浄化装置。

【請求項１７】前記排気ガスフィルターを収納し、かつ一側部に形成された排気ガス流入口と他側部に形成された排気ガス流出口とを有するケースと、を備えたことを特徴とする請求項１６に記載の排気ガス浄化装置。

【請求項１８】前記ケースの近傍に配設された送風手段を有することを特徴とする請求項１７に記載の排気ガス浄化装置。

【請求項１９】請求項１６乃至１８の内いずれか１に記載の排気ガス浄化装置が、エンジン直下のマニホールド部近傍に配設されていることを特徴とする排気ガス浄化システム。

【請求項２０】前記マニホールド部と前記ケースの排気ガス流入口との接続管の外周に断熱材を備えていることを特徴とする請求項１９に記載の排気ガス浄化システム。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、内燃機関の排気ガスを浄化する排気ガス浄化用触媒の製造方法、及び排気ガス浄化用触媒を用いた排気ガス浄化装置、特にディーゼル機関の排気ガスに含まれる一酸化炭素、炭化水素、パティキュレートを酸化燃焼して浄化する排気ガス浄化用触媒の製造方法、及び排気ガス浄化用触媒を用いた排気ガスフィルター及び排気ガス浄化装置並びに排気ガス浄化システムに関するものである。

【０００２】

【従来の技術】内燃機関からの排気ガスが大気中に安全に放出されるように浄化処理することは、環境保全上望

ましいことである。ガソリンエンジンについては、排気ガスの厳しい規制と、それに対する技術の進歩、具体的にはいわゆる三元触媒の出現と更なる改良により、排気ガス中の有害物質は確実に減少している。しかし、ディーゼルエンジンについては、その特異な原理とパティキュレートと呼ばれる有害成分の存在により、規制がガソリンエンジンに比べて緩く、又、規制が緩いこともあいまって、有害物質排出抑制のための技術開発もガソリンエンジンに比べて大きく遅れており、確実に浄化できる排気ガス浄化用触媒、及び排気ガス浄化用触媒を用いた排気ガス浄化装置の開発が望まれている。

【０００３】現在までに開発されているディーゼルエンジンからの排気ガスを浄化する触媒としては、三元触媒と基本的に同じ構成であるオーブン型ＳＯＦ（Ｓｏｌｕｂｌｅ　Ｏｒｇａｎｉｃ　Ｆｒａｃｔｉｏｎ；可溶性有機成分、高沸点の炭化水素）分解触媒が知られている。公知の技術である含浸法により、調製されたオーブン型ＳＯＦ分解触媒では、例えば特開平１－１７１６２６号公報に開示されているように、ガソリンエンジンと同様に触媒活性成分である白金族金属等の金属微粒子が高比表面積の担体上に分散、担持されており、一酸化炭素や炭化水素とともにディーゼルパティキュレート中のＳＯＦが酸化分解して浄化される。高比表面積の担体としては、耐熱性等を考慮してγ－アルミナ等の活性アルミナ又はアルカリ金属や希土類が添加された活性アルミナ等が用いられている。このオーブン型ＳＯＦ分解触媒は、ドライスーツの除去率が低いという欠点があるが、ドライスーツの量はディーゼルエンジンそのもののメカニカルな改良や燃料自体の改良によって低減することが可能であり、かつ再生処理装置が不要という大きなメリットがあるため、今後の一層の技術の向上が期待されている。ところが、オーブン型ＳＯＦ分解触媒も排気ガス中に含まれる触媒被毒物質により触媒活性が低下する。すなわち、ディーゼルエンジンに使用する軽油には、現在のところ０．４０～０．４５重量%の硫黄分が含有され、長期規制実施後も０．０５重量%程度の硫黄分が含有されるため、エンジンの燃焼の際に硫黄分が酸化して硫黄酸化物となり、これが触媒活性成分と作用して、触媒活性が低下する。

【０００４】そこで根本的な触媒活性を向上させるために、従来の含浸法にクエン酸等の多塩基カルボン酸等を添加した系で調製する方法が、特公平６０－８８６３号公報に開示されている。球状やペレット状の担体の外表面上に触媒活性成分を担持することで、触媒成分の表面から内部への進入深さを制御して、触媒活性を向上させるものであるが、触媒成分自体の粒子径や分布状態を制御するまでには至っておらず、従って、硫黄酸化物による被毒受けて、触媒活性は経時的に低下し耐久性に欠ける。

【０００５】【発明が解決しようとする課題】以上のように、従来の排気ガス浄化用触媒では、硫黄酸化物との作用を効果的に防止することが十分になされていないため、硫黄酸化物による耐被毒性に乏しく、経時的に触媒性能が劣化し、自動車用触媒としての寿命が短いという課題がを有していた。

【０００６】本発明は上記従来の課題を解決するもので、内燃機関、特にディーゼルエンジンからの排気ガスに含まれる硫黄酸化物と排気ガス浄化用触媒との作用を防止することによって、硫黄酸化物に対する耐被毒性に優れた排気ガス浄化用触媒の製造方法の提供、及び硫黄酸化物に対する耐被毒性に優れるとともに信頼性や耐久性に優れた排気ガスフィルターの提供、及び高浄化性で信頼性や耐久性に優れた排気ガス浄化装置の提供、及び高い捕集率でＳＯＦ等を捕集し信頼性や耐久性に優れた排気ガス浄化システムの提供を目的としている。

【０００７】【課題を解決するための手段】前記課題を解決するため、本発明の排気ガス浄化用触媒の製造方法は、触媒活性成分を触媒担体上に含浸担持する担持工程において、触媒活性成分と担体を混合した混合溶液中に、分子の構成成分に硫黄を含む、触媒活性成分と錯体を形成する錯化剤を適量添加し、前記混合溶液を撹拌、乾燥後、還元雰囲気中、所定の温度で焼成し、更に酸化雰囲気中、所定の温度で焼成する。また、望ましくは更に、硫黄酸化物を含む酸化雰囲気中、所定の温度で焼成する構成を有する。これにより、ディーゼルエンジンからの排気ガス中に含まれる一酸化炭素、炭化水素、パティキュレート中のＳＯＦを酸化燃焼して浄化する際に、触媒毒である硫黄酸化物と触媒活性成分との作用を防止することが可能となり、硫黄酸化物に対する耐被毒性に優れた、長寿命な排気ガス浄化用触媒を低原価で量産できる排気ガス浄化用触媒の製造方法を実現することができる。

【０００８】また、本発明の排気ガスフィルターは、セラミック製のハニカム構造体の各セル壁に担持された前記排気ガス浄化用触媒を備えた構成を有している。これにより、排気ガス中の硫黄化合物に対する耐被毒性に優れ高い触媒活性を長期間維持し信頼性や耐久性に優れた排気ガスフィルターを実現できる。

【０００９】また、本発明の排気ガス浄化装置は、本発明の排気ガス浄化用触媒の製造方法に基ずき作製した触媒、前記触媒を担持するための耐熱性ハニカム構造体、触媒付き耐熱性ハニカム構造体を収納するためのケースを備えた構成よりなる。これらの構成により、ディーゼルエンジンからの排気ガス中に含まれる一酸化炭素、炭化水素、パティキュレート中のＳＯＦを酸化燃焼して浄化する際に、触媒毒である硫黄酸化物と触媒活性成分との作用を防止することが可能となり、硫黄酸化物に対する耐被毒性に優れ耐久性に優れた排気ガス浄化装置を提供することができる。

【００１０】また、本発明の排気ガス浄化システムは、前記排気ガス浄化装置をディーゼルエンジン直下のマニホールド部近傍に配設した構成を有している。これにより、高濃度のＳＯＦ等を含んだ排気ガスを高い浄化率で浄化することができるとともに長期間高い触媒活性を維持し信頼性や耐久性に優れた排気ガス浄化システムを実現できる。

【００１１】

【発明の実施の形態】本発明の請求項１に記載の排気ガス浄化用触媒の製造方法は、多孔性無機物からなる担体と、前記担体の表面上に担持された貴金属、卑金属、金属酸化物の内のいずれか一種類以上からなる触媒活性成分と、を有する排気ガス浄化用触媒の製造方法であって、前記担体に前記触媒活性成分を担持する担持工程を有し、前記担持工程で使用される前記触媒活性成分に前記触媒活性成分と錯体を形成する錯化剤が添加されている構成を有している。この構成により、触媒活性成分の微粒子化及び高分散化が可能となり、反応に寄与する触媒の表面積が著しく大きくなり活性が向上するという作用を有する。

【００１２】ここで、多孔性無機物としては、高比表面積を有するもので、活性アルミナの他に、α－アルミナ、シリカ、シリカ－アルミナ、チタニア、マグネシア、ジルコニア等の多孔体も用いることができる。尚、多孔性無機物の表面に他の酸化物薄膜をコーティングした多孔性無機物質を用いても良い。酸化物薄膜を形成する方法としては、含浸法、浸漬法等により担体表面に被覆した後、乾燥し、焼成する方法等が用いられるが、前記酸化物の出発原料は各金属のアルコキシド、各金属塩等を用いることができる。

【００１３】触媒活性成分としては、白金、パラジウム、ロジウム、オスミウム、イリジウム、ルテニウム、金、銀等の貴金属、リチウム、ナトリウム、カリウム、ルビジウム、セシウム、マグネシウム、カルシウム、ストロンチウム、バリウム、スカンジウム、イットリウム、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、タンタル、クロム、モリブデン、タングステン、マンガン、テクネチウム、レニウム、鉄、コバルト、ニッケル、銅、亜鉛、錫等の卑金属、酸化銅、酸化ニッケル、酸化コバルト、酸化ランタン、酸化セリウム、酸化鉄、酸化バナジウム、酸化亜鉛、酸化クロム、酸化アルミニウム、酸化カルシウム、酸化バリウム、酸化金、酸化銀、酸化白金、酸化パラジウム、酸化タリウム、酸化トリウム、酸化チタン、酸化珪素、酸化マグネシウム、酸化モリブデン、酸化イットリウム、酸化ジルコニウム、酸化ベリリウム等の金属酸化物、ABO_3（Aはランタン、セリウム等の希土類の少なくとも１種類以上の元素、Bはクロム、マンガン、鉄、コバルト等の遷移金属、リチウム、ナトリウム等のアルカリ金属、ストロンチウム、バリウム等のアルカリ土類金属、白金、パラジウム等の貴金属の内の少なくとも１種類以上の元素）を基本構造とするペロブスカイト型複合酸化物、スピネル型複合酸化物、ペロブスカイト・スピネル複合酸化物等の金属複合酸化物の内のいずれか一種類以上が用いられる。

【００１４】本発明の請求項２に記載の排気ガス浄化用触媒の製造方法は、請求項１において、触媒活性成分と錯体を形成する錯化剤が、触媒活性成分に配位する原子として硫黄を含有する構成を有している。この構成により、硫黄原子で配位することにより、より物性の安定した金属錯体を形成し、また、配位子となる硫黄の原子半径が他の錯化剤の配位子の原子半径よりも大きいことから、より立体的な金属錯体を形成することができ、その結果、金属イオン同士間の距離が三次元的に均一となり、担体表面における触媒活性成分の分散性が均一となるという作用を有する。

【００１５】本発明の請求項３に記載の排気ガス浄化用触媒の製造方法は、請求項１又は２において、触媒活性成分と錯体を形成する錯化剤がジエチルジチオカルバミン酸誘導体の塩からなる構成を有している。この構成により、触媒活性成分がジエチルジチオカルバミン酸誘導体の塩に含まれる２つの硫黄原子と錯体を形成し、この際、硫黄の原子半径が大きいことから立体的な錯体を形成し、担体表面に担持される際にある一定の距離をもって高分散に担持されるという作用を有する。

【００１６】本発明の請求項４に記載の排気ガス浄化用触媒の製造方法は、請求項３において、前記ジエチルジチオカルバミン酸誘導体の塩がジエチルジチオカルバミン酸ジエチルアンモニウムである構成を有している。この構成により、ジエチルジチオカルバミン酸ジエチルアンモニウムに含まれる２つの硫黄原子と錯体を形成し、この際、硫黄の原子半径が大きいことから立体的な錯体を形成し、担体表面に担持される際にある一定の距離をもって高分散に担持するとともに、２つのジエチルアンモニウムにより安定した錯体が形成されるという作用を有する。

【００１７】本発明の請求項５に記載の排気ガス浄化用触媒の製造方法は、請求項１乃至４の内いずれか１において、前記錯化剤の添加量ａが触媒活性成分の添加量ｂに対して、モル比（ａ／ｂ）が１～１０、好ましくは３～５に調整された構成を有している。この構成により、金属錯体が効率的に形成されるという作用を有する。

【００１８】ここで、モル比（ａ／ｂ）が３よりも小さくなるにつれ触媒活性成分の種類にもよるが、金属錯体の形成が不十分で触媒活性成分の分散性が不均一になる傾向が認められ、特にモル比（ａ／ｂ）が１未満ではこの傾向が著しく、また、モル比（ａ／ｂ）が５よりも大きくなるにつれ触媒活性成分の種類にもよるが、均一な分散に関与しないものが多くなり触媒活性も殆ど平衡に達する傾向が認められ、特にモル比（ａ／ｂ）が１０を

超えるとこの傾向が著しくなるので、いずれも好ましくない。

【００１９】本発明の請求項６に記載の排気ガス浄化用触媒の製造方法は、請求項１乃至５の内いずれか１において、前記担持工程が触媒活性成分と担体と錯化剤の混合溶液のｐＨを０．１～２．０、好ましくは１．５～２に調整して行われる構成を有している。この構成により、混合溶液中の触媒活性成分の金属塩の溶解度が向上し、錯化剤の錯体形成が容易になり、触媒としたときの触媒活性成分の均一分散性が向上するという作用を有する。

【００２０】本発明の請求項７に記載の排気ガス浄化用触媒の製造方法は、請求項６において、前記混合溶液のｐＨを調整するためのｐＨ調整剤として塩素を含有しない酸を用いる構成を有している。この構成により、触媒中に残留塩素が残らないようにし、塩素による触媒の活性低下を抑制する作用を有する。

【００２１】本発明の請求項８に記載の排気ガス浄化用触媒の製造方法は、請求項１乃至７の内いずれか１において、触媒を担持した担体を焼成する焼成工程が、酸化雰囲気下で焼成する酸化焼成工程を有する構成を備えている。これにより、還元焼成は触媒成分を金属の形で担体上に担持し、酸化焼成により酸素に接触させることで酸化雰囲気下での耐熱性を確保することができるという作用を有する。

【００２２】尚、酸化焼成工程の前工程として、触媒を担持した担体を還元雰囲気下で焼成する還元焼成工程を設けるのが好ましい。還元焼成により触媒成分は、金属状態で担体上に担持される。

【００２３】本発明の請求項９に記載の排気ガス浄化用触媒の製造方法は、請求項８において、前記酸化焼成工程が、酸化雰囲気中所定の温度で焼成を行った後に、更に硫黄酸化物ガスを含む酸化雰囲気下所定の温度で焼成を行う構成を有している。これにより、触媒活性成分のうちの酸化反応に不活性な成分を、酸化反応に活性な成分に変化させる作用を有する。ここで、硫黄酸化物ガスの濃度としては、１０～１００００ｐｐｍが用いられる。硫黄酸化物ガスは触媒活性成分と当量導入すれば充分であり、「温度×時間」で決まるが上記範囲内が好適に用いられる。

【００２４】本発明の請求項１０に記載の排気ガス浄化用触媒の製造方法は、請求項８又は９において、前記酸化焼成工程が、酸化雰囲気中所定の温度で焼成を行った後に、更に硫黄酸化物ガス及び水蒸気を含む酸化雰囲気下で所定の温度で焼成を行う構成を有している。これにより、触媒成分の塩の残留成分を除去するという作用を有する。また、これにより触媒活性成分が被毒されるのを防止するという作用を有する。更に、触媒活性成分の内の酸化反応に不活性であったものを、酸化反応に活性なものに変化させる作用を有する。ここで、水蒸気の濃度としては、１～５０ｖｏｌ％が用いられる。この範囲の水蒸気濃度により系内の残留成分を有効に除去し触媒活性成分の残留成分による被毒を防止し、所期の触媒活性を与えるという作用を有する。

【００２５】本発明の請求項１１に記載の排気ガス浄化用触媒の製造方法は、請求項８乃至１０において、前記酸化焼成工程の硫黄酸化物ガスの存在下又は硫黄酸化物ガス及び水蒸気を含む酸化雰囲気下での焼成温度が、１００～１０００℃、好ましくは４００～５００℃で行う構成を有している。これにより、触媒活性成分の内の酸化反応に不活性であったものを、酸化反応に活性なものに変化させる作用を有する。

【００２６】ここで、焼成温度が４００°Ｃよりも低くなるにつれ触媒活性成分の内の酸化反応に不活性であったものを、酸化反応に活性なものに変化させるという効果が得られ難くなる傾向が認められ、また、５００℃よりも高くなるにつれ硫黄酸化物ガスが安定に触媒成分と反応を行えず、触媒活性が不活性になる傾向が認められるので、いずれも好ましくない。

【００２７】本発明の請求項１２に記載の排気ガス浄化用触媒の製造方法は、請求項８乃至１１の内いずれか１において、前記酸化焼成工程の硫黄酸化物ガスの存在下又は硫黄酸化物ガス及び水蒸気を含む酸化雰囲気下での焼成時間が１～１００時間、好ましくは２０～３０時間である構成を有している。これにより、触媒活性成分の内の酸化反応に不活性であったものを、酸化反応に活性なものに変化させる作用を有する。

【００２８】ここで、焼成時間が２０時間よりも短くなるにつれ所期の触媒活性が得られ難い傾向が認められ、また、３０時間よりも長くなるにつれ触媒活性が平衡に達する傾向が認められるので、いずれも好ましくない。

【００２９】本発明の請求項１３に記載の排気ガス浄化用触媒の製造方法は、請求項１乃至１２の内いずれか１において、前記担体がシリカをコーティングした活性アルミナである構成を有している。これにより、硫黄酸化物ガスを含む酸化雰囲気中で熱処理を行う際にも、担体と硫黄酸化物との反応が抑制され、処理に伴う比表面積の低下を防止することができるという作用を有する。

【００３０】本発明の請求項１４に記載の排気ガス浄化用触媒の製造方法は、請求項１３において、前記活性アルミナの比表面積が５０～２００m^2／ｇ、中心粒子径が０．３～１０μｍ、細孔容積が０．４ｃｃ／ｇ～１ｃｃ／ｇを有する構成を有している。これにより、触媒活性成分が均一に分散し、かつ、微粒化した状態で担持でき広い表面積を得ることができるという作用を有する。

【００３１】本発明の請求項１５に記載の発明は、本体が円柱状又は角柱状に形成され軸方向に多数のセルを有し前記各セルの両端面のいずれか一方を封止剤で封止されたセラミック製のハニカム構造体と、前記ハニカム構造体のセル壁に担持された請求項１乃至１４の内いずれ

か１に記載の排気ガス浄化用触媒の製造方法で作製された排気ガス浄化用触媒と、を備えた構成を有している。これにより、耐被毒性に優れた触媒活性成分を均一に分散した担体をセル壁に担持しているので、排気ガス中のＳＯＦ等を高効率で分解し浄化する事ができるとともに、耐久性、信頼性を向上できるという作用を有する。

【００３２】本発明の請求項１６に記載の発明は、請求項１５に記載された排気ガスフィルターと、前記排気ガスフィルターを加熱する加熱手段と、を有する構成を有している。これにより排気ガス浄化用触媒を加熱することにより、低温の排気ガスも高温の排気ガスと同様に高効率で浄化できるという作用を有する。

【００３３】加熱手段としては電気ヒーター、バーナー、マイクロ波等が用いられる。本発明の請求項１７に記載の発明は、請求項１６に記載の発明において、前記排気ガスフィルターを収納し、かつ一側部に形成された排気ガス流入口と他側部に形成された排気ガス流出口とを有するケースと、を備えた構成を有している。

【００３４】これにより、排気ガス浄化用触媒をケースに収納し、ケースに排気ガスの流入・流出口を設けたことによって、ディーゼルエンジンの排気系に取り付けることができるという作用を有する。

【００３５】ケースとしては耐酸化性に優れた金属、セラミックス等が用いられる。本発明の請求項１８に記載の発明は、請求項１７に記載の発明において、前記ケースの近傍に配設された送風手段を有する構成を有している。これにより、ディーゼルエンジンの排気系における低温の排気ガスを加熱流体にして排気ガス浄化用触媒に吹き付けることにより、低温の排気ガスの浄化効率が向上するという作用を有する。

【００３６】送風手段としてはブロアー、コンプレッサー等が用いられる。本発明の請求項１９に記載の発明は、請求項１６乃至１８の内いずれか１に記載の排気ガス浄化装置が、エンジン直下のマニホールド部近傍に配設された構成を有している。これにより、排気ガスの温度低下が抑制されることにより、排気ガスの浄化効率が向上するという作用を有する。

【００３７】本発明の請求項２０に記載の発明は、請求項１９において、前記マニホールド部と前記ケースの排気ガス流入口との接続管の外周に断熱材を備えてた構成を有している。これにより、排気ガスの温度低下を防止することにより、排気ガスの浄化効率が向上するという作用を有する。

【００３８】接続管としては耐酸化性に優れた金属等が用いられ、断熱材としてはアスベスト、ガラス綿、スラグウール等が用いられる。

【００３９】以下、本発明の実施の形態の具体例について、図面を用いて説明する。

（実施の形態１）図１は本発明の実施の形態１における排気ガス浄化用触媒の製造方法の工程図である。実施の形態１における排気ガス浄化用触媒の製造方法の製造工程は秤量工程１、含浸工程２、乾燥工程３及び焼成工程４の４つの工程からなる。含浸工程２において、触媒活性成分と錯体を形成する錯化剤を混合するとともに、担体に含浸を行う。焼成工程４においては、先ず最初に還元雰囲気で焼成を行い、次に酸化雰囲気で焼成を行う。また、必要に応じて更に特定成分を含有した酸化雰囲気中で焼成する。

【００４０】以下に実施例を基に更に詳しく説明する。

【００４１】

【実施例】

（実施例１）

＜担体の調製＞活性アルミナ粉末（住友化学工業製）のエタノール溶液１００ｗｔ部に、テトラエトキシシラン（関東化学製）を１０ｗｔ部を添加し、そのまま一昼夜撹拌混合しながら、エタノールを蒸発させ乾固させた。固まりを乳鉢で粉体状にした後、８００℃で５時間焼成してシリカコーティング活性アルミナからなる担体を得た。

【００４２】＜触媒活性成分の溶液の調製＞濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部、ジエチルジチオカルバミン酸ジエチルアンモニウム（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部を混合し触媒活性成分の溶液を得た。

【００４３】＜排気ガスフィルターの製造＞得られたシリカコーティング活性アルミナ粉末を１０ｗｔ部、硝酸アルミニウム（和光純薬工業製）を１ｗｔ部、アルミナゾル（日産化学製）を５ｗｔ部及び蒸留水１００ｗｔ部を混合して得たスラリー中にコージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１分間浸漬した後、引き上げて、エアーブロー等により余分なスラリーを吹き払った後、１２０℃で２時間乾燥する。次いで８００℃で５時間焼成し、ムライト製ハニカムフィルターの表面上にシリカコーティング活性アルミナを担持した。次に、調製後一昼夜放置した触媒活性成分の溶液に、得られたハニカムフィルターを１０分間浸漬した後引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥する。次いで６００℃で２時間還元雰囲気中で焼成した後、更に８００℃で５時間酸化雰囲気中で焼成し、更に４５０℃で５時間酸化雰囲気中で焼成して担体の表面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００４４】（実施例２）実施例１で得られたシリカコーティング活性アルミナを１００ｗｔ部と、実施例１で得られた触媒活性成分の溶液１００ｗｔ部とを混合後、一昼夜撹拌した後、この混合溶液に増粘剤を１０ｗｔ部を添加し混合する。次いで、この混合溶液に、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１

０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で２時間焼成し、更に８００℃で５時間酸化雰囲気中で焼成して、更に４５０℃で５時間酸化雰囲気中で焼成して担体の表面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００４５】（実施例３）実施例１で得られたシリカコーティング活性アルミナを１００ｗｔ部と、実施例１で得られた触媒活性成分の溶液１００ｗｔ部とを混合後、一昼夜撹拌した後、この混合溶液に増粘剤を１０ｗｔ部を添加し混合後、一昼夜撹拌した後、１２０℃で２時間乾燥してから６００℃で２時間焼成し、担体上に触媒活性成分を担持し、排気ガス浄化用触媒とした。次に、前記排気ガス浄化用触媒１００ｗｔ部と増粘剤１０ｗｔ部及び蒸留水２００ｗｔ部を混合して調製したスラリーに、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬し、次いで余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから、更に前記ハニカムフィルターを８００℃で５時間酸化雰囲気中で焼成し、次いで、更に４５０℃で５時間酸化雰囲気中で焼成して前記ハニカムフィルターの表面に触媒を担持した担体をコーティングした排気ガスフィルターを得た。

【００４６】（実施例４）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、硝酸アルミニウム（和光純薬工業製）を１ｗｔ部、アルミナゾル（日産化学製）を５ｗｔ部及び蒸留水１００ｗｔ部とを混合して得られたスラリー中に、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１分間浸漬してから引き上げて、エアーブロー等により余分なスラリーを吹き払った後、１２０℃で２時間乾燥した後、更に前記ハニカムフィルターを８００℃で５時間焼成し、表面上にシリカコーティング活性アルミナを担持したムライト製ハニカムフィルターを作製した。次に、実施例１で得られた触媒活性成分の溶液１００ｗｔ部に一昼夜放置した後、得られたハニカムフィルターをこの触媒活性成分の溶液に、１０分間浸漬した後引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥する。次いで６００℃で２時間還元雰囲気中で焼成した後、更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物を含有する酸化雰囲気中で焼成して、担体の表面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００４７】（実施例５）実施例１で得られたシリカコーティング活性アルミナを１００ｗｔ部と、実施例１で得られた触媒活性成分の溶液１００ｗｔ部とを混合して得た混合水溶液を一昼夜撹拌した後、この混合水溶液に、増粘剤を１０ｗｔ部添加した後、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で還元雰囲気中２時間焼成し、更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物を含有する酸化雰囲気中４５０℃で焼成して、担体の表面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００４８】（実施例６）実施例１で得られたシリカコーティング活性アルミナを１００ｗｔ部と、実施例１で得られた触媒活性成分の溶液１００ｗｔ部とを混合した後、一昼夜撹拌し、次いで１２０℃で２時間乾燥してから６００℃で２時間焼成し、担体上に触媒活性成分を担持し、触媒とした。次に、前記触媒１００ｗｔ部と増粘剤１０ｗｔ部及び蒸留水２００ｗｔ部を混合して所定の粘度に調製したスラリーに、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから更に８００℃で５時間酸化雰囲気中で焼成した後、更に硫黄酸化物１０００ｐｐｍを含有する酸化雰囲気中４５０℃で焼成して、前記ハニカムフィルターの表面に触媒を担持した担体をコーティングした排気ガスフィルターを得た。

【００４９】（実施例７）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、硝酸アルミニウム（和光純薬工業製）を１ｗｔ部、アルミナゾル（日産化学製）を５ｗｔ部及び蒸留水１００ｗｔ部とを混合して得られたスラリー中に、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１分間浸漬してから引き上げて、エアーブロー等により余分なスラリーを吹き払った後、１２０℃で２時間乾燥してから８００℃で５時間焼成し、ムライト製ハニカムフィルターの表面上にシリカコーティング活性アルミナを担持した。次に、実施例１で得られた触媒活性成分の溶液１００ｗｔ部を一昼夜放置した後、この触媒活性成分の溶液に、得られたハニカムフィルターを１０分間浸漬した後引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥する。次いで、前記ハニカムフィルターを６００℃で２時間還元雰囲気中で焼成した後、更に８００℃で５時間酸化雰囲気中で焼成し、更に硫黄酸化物１０００ｐｐｍ及び水蒸気１０ｖｏｌ％を含有する酸化雰囲気中で焼成して、担体の表面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００５０】（実施例８）実施例１で得られたシリカコーティング活性アルミナを１００ｗｔ部と、実施例１で得られた触媒活性成分の溶液１００ｗｔ部とを混合した後、一昼夜撹拌し、この混合溶液に１０ｗｔ部の増粘剤を添加した後、コージェライト製ハニカムフィルター

（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で還元雰囲気中２時間焼成し、更に前記ハニカムフィルターを８００℃で５時間酸化雰囲気中で焼成した後、更に硫黄酸化物１０００ｐｐｍ及び水蒸気１０ｖｏｌ％を含有する酸化雰囲気中４５０℃で焼成して、担体の上面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００５１】（実施例９）実施例１で得られたシリカコーティング活性アルミナを１００ｗｔ部と、実施例１で得られた触媒活性成分の溶液１００ｗｔ部とを混合した後、一昼夜撹拌し、次いで１２０℃で２時間乾燥してから６００℃で２時間焼成し、担体上に触媒活性成分を担持し、触媒とした。次に、前記触媒と増粘剤及び蒸留水を混合して所定の粘度に調製したスラリーに、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから更に前記ハニカムフィルターを８００℃で５時間酸化雰囲気中で焼成した後、更に硫黄酸化物１０００ｐｐｍ及び水蒸気１０ｖｏｌ％を含有する酸化雰囲気中４５０℃で焼成して、前記ハニカムフィルターの表面に触媒を担持した担体をコーティングした排気ガスフィルターを得た。

【００５２】（比較例１）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、硝酸アルミニウム（和光純薬工業製）を１ｗｔ部、アルミナゾル（日産化学製）を５ｗｔ部及び蒸留水１００ｗｔ部とを混合して得られたスラリー中に、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１分間浸漬してから引き上げて、エアーブロー等により余分なスラリーを吹き払った後、１２０℃で２時間乾燥してから８００℃で５時間焼成し、ムライト製ハニカムフィルターの表面上にシリカコーティング活性アルミナを担持した。次に、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部、とクエン酸（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部とを混合後、一昼夜放置した混合水溶液に、前記ハニカムフィルターを１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で２時間還元雰囲気中焼成し、更に８００℃で５時間酸化雰囲気中で焼成して、更に４５０℃で５時間酸化雰囲気中で焼成して前記ハニカムフィルターの上面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００５３】（比較例２）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部とクエン酸（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部とを混合後、一昼夜撹拌し、この混合溶液に１０ｗｔ部の増粘剤を添加した後、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で２時間焼成し、更に８００℃で５時間酸化雰囲気中で焼成して、更に４５０℃で５時間酸化雰囲気中で焼成して前記ハニカムフィルターの上面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００５４】（比較例３）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部、クエン酸（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部を混合した後、一昼夜撹拌し、次いで１２０℃で２時間乾燥してから６００℃で２時間焼成し、担体上に触媒活性成分を担持し、触媒とした。次に、前記触媒１００ｗｔ部と増粘剤１０ｗｔ部及び蒸留水２００ｗｔ部を混合して所定の粘度に調製したスラリーに、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから更に８００℃で５時間酸化雰囲気中で焼成し、前記ハニカムフィルターの表面に触媒を担持した担体をコーティングし、排気ガスフィルターを得た。

【００５５】（比較例４）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、硝酸アルミニウム（和光純薬工業製）を１ｗｔ部、アルミナゾル（日産化学製）を５ｗｔ部及び蒸留水１００ｗｔ部とを混合して得られたスラリー中に、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１分間浸漬してから引き上げて、エアーブロー等により余分なスラリーを吹き払った後、１２０℃で２時間乾燥してから８００℃で５時間焼成し、ムライト製ハニカムフィルターの表面上にシリカコーティング活性アルミナを担持した担体を作製した。次に、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部、とクエン酸（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部とを混合後、一昼夜放置した混合水溶液に、担体を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で２時間還元雰囲気中焼成し、更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物を含有する酸化雰囲気中で焼成して、担体の表面にパラジウム及び白金並びにこれらの金属の酸化物から

なる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００５６】（比較例５）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部とクエン酸（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部とを混合後、一昼夜撹拌し、この混合溶液に所定量の増粘剤を添加した後、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で２時間焼成し、更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物を含有する酸化雰囲気中４５０℃で焼成して、担体の表面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００５７】（比較例６）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部、ジエチルジチオカルバミン酸ジエチルアンモニウム（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部とを混合した後、一昼夜撹拌し、次いで１２０℃で２時間乾燥してから６００℃で２時間焼成し、担体上に触媒活性成分を担持し、触媒とした。次に、前記触媒と増粘剤及び蒸留水を混合して所定の粘度に調製したスラリーに、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物を含有する酸化雰囲気中４５０℃で焼成して、前記ハニカムフィルターの表面に触媒を担持した担体をコーティングした排気ガスフィルターを得た。

【００５８】（比較例７）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、硝酸アルミニウム（和光純薬工業製）を１ｗｔ部、アルミナゾル（日産化学製）を５ｗｔ部及び蒸留水１００ｗｔ部とを混合して得られたスラリー中に、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１分間浸漬してから引き上げて、エアーブロー等により余分なスラリーを吹き払った後、１２０℃で２時間乾燥してから８００℃で５時間焼成し、ムライト製ハニカムフィルターの表面上にシリカコーティング活性アルミナを担持した。次に、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部、とクエン酸（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部とを混合後、一昼夜放置した混合水溶液に、前記ハニカムフィルターを１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で２時間還元雰囲気中焼成し、更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物及び水蒸気を含有する酸化雰囲気中で焼成して、担体の表面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００５９】（比較例８）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部とクエン酸（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部とを混合後、一昼夜撹拌し、この混合溶液に増粘剤１０ｗｔ部を添加した後、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから６００℃で２時間焼成し、更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物１０００ｐｐｍ及び水蒸気１０ｖｏｌ％を含有する酸化雰囲気中４５０℃で焼成して、担体の上面にパラジウム及び白金並びにこれらの金属の酸化物からなる触媒活性成分を担持させ、排気ガスフィルターを得た。

【００６０】（比較例９）実施例１で得られたシリカコーティング活性アルミナを１０ｗｔ部、濃度９７～１０２の硝酸パラジウム（和光純薬工業製）０．１１ｗｔ部と、ジニトロジアミノ白金（田中貴金属製）０．１２ｗｔ部、ジエチルジチオカルバミン酸ジエチルアンモニウム（和光純薬工業製）０．７０ｗｔ部と蒸留水１００ｗｔ部を混合した後、一昼夜撹拌し、次いで１２０℃で２時間乾燥してから６００℃で２時間焼成し、担体上に触媒活性成分を担持し、触媒とした。次に、前記触媒と増粘剤及び蒸留水を混合して所定の粘度に調製したスラリーに、コージェライト製ハニカムフィルター（例えば、ＮＧＫ製）を１０分間浸漬してから引き上げ、余分な溶液をエアーブロー等で吹き払った後、１２０℃で２時間乾燥してから更に８００℃で５時間酸化雰囲気中で焼成し、更に前記ハニカムフィルターを硫黄酸化物及び水蒸気を含有する酸化雰囲気中４５０℃で焼成して、前記ハニカムフィルターの表面に触媒を担持した担体をコーティングした排気ガスフィルターを得た。

【００６１】＜触媒の活性評価＞実施例１～９及び比較例１～９における排気ガス浄化用触媒の活性評価試験を行った。図２は、触媒活性評価試験に用いた固定床流通系反応装置の概略図である。図２において、硫黄酸化物を１００ｐｐｍ含有した窒素ガス４１、乾燥空気４２、ＳＯＦ４３は気体用流量調製器４４、４５と液体用流量調製器４６のそれぞれによって所定の流量に調節された後、気化器４７においてＳＯＦ４３が所定濃度で気化さ

れるとともに硫黄酸化物を１００ｐｐｍ含有した窒素ガス４１及び乾燥空気４２と混合される。この混合ガスは石英管４８内に導入され、石英管４８内に置かれた排気ガス浄化用触媒４９によって浄化される。尚、排気ガス浄化用触媒４９の前後には石英ウール５０が配置され、石英管４８は電気炉５１内に設置されている。浄化された混合ガスはＮＤＩＲ方式の一酸化炭素、二酸化炭素ガス分析計５２に導入されて一酸化炭素濃度及び二酸化炭素濃度を検知した後、酸素センサ５３に導入されて酸素＊濃度が測定される。尚、触媒活性評価試験は、混合ガスの酸素分圧１２％、空間速度３００００／ｈ-1、ＳＯＦ濃度３００ｐｐｍ、硫黄酸化物ガス濃度１００ｐｐｍ、電気炉内温度２５０℃の条件で触媒活性の経時変化を測定した。以上の方法により計測された一酸化炭素濃度、二酸化炭素濃度から、（数１）により燃焼率を算出した。

【００６２】

【数１】

$$\text{ＳＯＦ燃焼率（％）}=\frac{PCO+PCO_2}{PC}\times 100$$

【００６３】（数１）において、ＰＣＯはＮＤＩＲ方式の一酸化炭素、二酸化炭素ガス分析計によって測定された一酸化炭素濃度の値、ＰＣＯ2はＮＤＩＲ方式の一酸化炭素、二酸化炭素ガス分析計によって測定された二酸化炭素濃度の値であり、ＰＣはＳＯＦが１００％燃焼した時の理論上のＣＯ又はＣＯ2の濃度である。燃焼率の経時変化を図３及び図４に示した。

【００６４】図３は実施例１～９における排気ガス浄化用触媒の触媒活性評価試験の燃焼率の経時変化を示す図であり、図４は比較例１～９における排気ガス浄化用触媒の触媒活性評価試験の燃焼率の経時変化を示す図である。図中、縦軸は（数１）より算出された燃焼率、横軸は上記実験条件で測定を行ったときの累積時間を示している。

【００６５】図３及び図４において、実施例１～３及び比較例１～３は、還元雰囲気焼成後に、酸化雰囲気焼成を行った場合を、実施例４～９及び比較例４～９については、還元雰囲気焼成後に、酸化雰囲気焼成を行い、次いで更に酸化硫黄ガスを含有する酸化雰囲気中で焼成を行った場合の結果である。この図３及び図４から明らかなように、何れの場合も初期活性は高い。実施例１～３の場合には、経時変化と共に活性がやや低下しているが、低下の程度は１０％程度であり、また、実施例４～９については、殆ど活性の低下が見られず、高活性で、長寿命であることが判る。一方、図４に示した比較例の結果を見てみると、比較例１～３は、比較的初期活性は高いものの、比較例４～９は、実施例に示した結果の初期活性に比べると、２０％程低く、また、経時変化後の活性を見てみると、２００時間経過後には、何れの比較例の燃焼率も４０％前後まで低下しており、低活性で、短寿命であることが判る。

【００６６】以上のように本実施例によれば、実施例１～３に示したように、混合工程において、触媒活性成分と錯体を形成する配位子を添加するだけでも、やや活性の低下が見られるものの、従来に比べて高活性で長寿命で耐久性に優れていることが分かる。更に、実施例４～９に示したように、焼成工程においても、還元雰囲気で焼成を行った後に、酸化雰囲気で焼成を行い、更に酸化硫黄ガスを含有する酸化雰囲気中で焼成する事により、従来例に比べるとはるかに高活性で長寿命を有する排気ガス浄化用触媒が得られることがわかる。

【００６７】また、本発明のいずれの実施例における排気ガス浄化用触媒についても、比較例における排気ガス浄化用触媒に比べて燃焼率の低下が小さいあるいは変化がなく、硫黄酸化物による耐被毒性に優れていることが判った。

【００６８】次に、本発明の排気ガス浄化用触媒の製造方法により得られた排気ガス浄化用触媒を使用した排気ガス浄化用フィルター、排気ガス浄化用装置、排気ガス浄化用システムについての実施の形態を示す。

【００６９】（実施の形態２）図５は本発明の排気ガス浄化用触媒の製造方法に基ずき作製した触媒を使用した実施の形態２における排気ガス浄化用触媒フィルターの断面図である。図５において、耐熱性ハニカム構造物５は排気ガス中の有害成分を捕集し、耐熱性ハニカム構造物５の表面に担持された多孔性無機物６は耐熱性ハニカム構造物５に高比表面積を提供し、多孔性無機物６の上面に担持された触媒活性成分７は、排気ガス中の一酸化炭素、炭化水素、パティキュレートを酸化燃焼により浄化する。尚、図２の矢印は排気ガスの流入・流出方向を示す。

【００７０】（実施の形態３）図６は本発明の実施の形態３における排気ガス浄化装置の断面図である。図６において、ケース８に形成された排気ガス流入口９より一酸化炭素、炭化水素、パティキュレートを含む排気ガスがケース８内に流入し、流入した排気ガスはケース８に収納された排気ガス浄化用触媒１０により浄化され、浄化された排気ガスはケース８に形成された排気ガス流出口１１より放出される。

【００７１】（実施の形態４）図７は本発明の実施の形態４における排気ガス浄化装置の断面図である。図７において、ケース１２に形成された排気ガス流入口１３より一酸化炭素、炭化水素、パティキュレートを含む排気ガスがケース１２内に流入し、ケース１２に収納された排気ガス浄化用触媒１４は加熱手段１６によって加熱され、加熱された排気ガス浄化用触媒１４によって流入し

た排気ガスが浄化され、浄化された排気ガスはケース１２に形成された排気ガス流出口１５より放出される。

【００７２】（実施の形態５）図８は本発明の実施の形態５における排気ガス浄化装置の断面図である。図８において、送風手段１７により一酸化炭素、炭化水素、パティキュレートを含む排気ガスが加速され、加速された排気ガスはケース１８に形成された排気ガス流入口１９よりケース１８内に流入し、流入した排気ガスはケース１８に設けられた加熱手段２０によって加熱され、加熱された排気ガスはケース１８内に収納された排気ガス浄化用触媒２１によって浄化され、浄化された排気ガスはケース１８に形成された排気ガス流出口２２より放出される。

【００７３】（実施の形態６）図９は本発明の実施の形態６における排気ガス浄化装置の断面図である。図９において、２３はエンジン、２４はエンジン直下のマニホールド部であり、エンジン２３より排気された一酸化炭素、炭化水素、パティキュレートを含む排気ガスは送風手段２５により加速され、加速された排気ガスはケース２６に形成された排気ガス流入口２７よりケース２６内に流入し、流入した排気ガスはケース２６に設けられた加熱手段２８によって加熱され、加熱された排気ガスはケース２６内に収納された排気ガス浄化用触媒２９によって浄化され、浄化された排気ガスはケース２６に形成された排気ガス流出口３０より放出される。尚、本実施の形態６においては、加熱手段２８又は加熱手段２８と送風手段２５がないシステムも可能である。

【００７４】（実施の形態７）図１０は本発明の実施の形態７における排気ガス浄化装置の断面図である。図１０において、３１はエンジン、３２はエンジン直下のマニホールド部であり、エンジン３１より一酸化炭素、炭化水素、パティキュレートを含む排気ガスは断熱材３３によって保温された接続管３４に導入され、導入された排気ガスは接続管３４内で送風手段３５により加速され、加速された排気ガスはケース３６に形成された排気ガス流入口３７よりケース３６内に流入し、流入した排気ガスはケース３６に設けられた加熱手段３８によって加熱され、加熱された排気ガスはケース３６内に収納された排気ガス浄化用触媒３９によって浄化され、浄化された排気ガスはケース３６に形成された排気ガス流出口４０より放出される。尚、本実施の形態においては、加熱手段３８又は加熱手段３８と送風手段３５がないシステムも可能である。

【００７５】

【発明の効果】以上のように、本発明の排気ガス浄化用触媒の製造方法に基ずいて作製した排気ガス浄化用触媒及びこれを用いた排気ガスフィルター及び排気ガス浄化装置並びに排気ガス浄化用システムによれば、以下のような優れた効果が得られる。

【００７６】請求項１に記載の発明によれば、触媒活性成分の微粒子化及び高分散化が可能となり、反応に寄与する触媒の表面積が著しく大きくすることができ高活性を有する排気ガス浄化用触媒を得ることができる。また、排気ガス中の硫黄酸化物による触媒活性成分の被毒を防止することにより、長期間排気ガスを高い浄化率で処理することが可能な排気ガス浄化用触媒を得ることができる。被毒による触媒機能の低下が防止された排気ガス浄化用触媒を用いることによって、触媒機能、耐久性、信頼性に優れた排気ガス浄化用触媒を得ることができる。という優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００７７】請求項２に記載の発明によれば、請求項１における効果に加え、触媒活性成分に硫黄原子で配位することにより、より物性の安定した金属錯体を形成し、また、配位子となる硫黄の原子半径が他の錯化剤の配位子の原子半径よりも大きいことから、より立体的な金属錯体を形成することができ、その結果、金属イオン同士間の距離が三次元的に均一となり、担体表面における触媒活性成分の分散性が均質化した排気ガス浄化用触媒を得ることができる。という優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００７８】請求項３に記載の発明によれば、請求項１又は２における効果に加え、触媒活性成分がジエチルジチオカルバミン酸誘導体の塩に含まれる２つの硫黄原子と錯体を形成し、この際、硫黄の原子半径が大きいことから立体的な錯体を形成し、担体表面に担持される際にある一定の距離をもって高分散に担持されるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００７９】請求項４に記載の発明によれば、請求項３における効果に加え、ジエチルジチオカルバミン酸ジエチルアンモニウムに含まれる２つの硫黄原子と錯体を形成し、この際、硫黄の原子半径が大きいことから立体的な錯体を形成し、担体表面に担持される際にある一定の距離をもって高分散に担持するとともに、２つのジエチルアンモニウムにより安定した錯体が形成されるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８０】請求項５に記載の発明によれば、請求項１乃至４の内いずれか１における効果に加え、金属錯体が効率的に形成されるので低原価で高活性の排気ガス浄化用触媒を得ることができるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８１】請求項６に記載の発明によれば、請求項１乃至５の内いずれか１における効果に加え、触媒活性成分の金属塩の溶解度が向上し、錯化剤の錯体形成が容易になり、触媒としたときの触媒活性成分の均一分散性が向上し排気ガス浄化用触媒の高活性が図れるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８２】請求項７に記載の発明によれば、請求項６における効果に加え、塩素による触媒の活性低下を抑制することができるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８３】請求項８に記載の発明によれば、請求項１乃至７の内いずれか１における効果に加え、排気ガス浄化用触媒の耐熱性を著しく向上させることができるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８４】請求項９に記載の発明によれば、請求項８における効果に加え、触媒活性成分のうちの酸化反応に不活性な成分を、酸化反応に活性な成分に変化させるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８５】請求項１０に記載の発明によれば、請求項８又は９における効果に加え、触媒成分の塩の対イオンが、触媒を担持する際に残留し、これにより触媒活性成分が被毒されることがあるが、水蒸気を添加したので、この残留成分を除去することができ、触媒活性成分の活性を向上させることができ、また触媒活性成分の内の酸化反応に不活性であったものを、酸化反応に活性なものに変化させるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８６】請求項１１に記載の発明によれば、請求項８乃至１０の内いずれか１における効果に加え、触媒活性成分の内、酸化反応に不活性な成分を酸化反応に活性な成分に変化させ高い触媒活性を得ることができるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８７】請求項１２に記載の発明によれば、請求項８乃至１１の内いずれか１における効果に加え、触媒活性成分の内、酸化反応に不活性な成分を酸化反応に活性な成分に変化させ高い触媒活性を得ることができるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８８】請求項１３に記載の発明によれば、請求項１乃至１２の内いずれか１における効果に加え、硫黄酸化物ガスを含む酸化雰囲気中で熱処理を行う際にも、担体と硫黄酸化物との反応が抑制され、処理に伴う比表面積の低下を防止することができ高い触媒活性を達成できるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００８９】請求項１４に記載の発明によれば、請求項１３における効果に加え、触媒活性成分を分散させ、かつ、微粒化した状態で担持できるという優れた効果を有する排気ガス浄化用触媒の製造方法を実現できる。

【００９０】請求項１５に記載の発明によれば、耐被毒性に優れた触媒活性成分を均一に分散した担体をセル壁に担持しているので、排気ガス中のＳＯＦ等を高効率で分解し浄化する事ができるとともに、耐久性に優れ、信頼性を向上させた排気ガスフィルターを実現できる。

【００９１】請求項１６に記載の発明によれば、排気ガス中の硫黄酸化物による触媒活性成分の被毒を防止することにより、長期間排気ガスを高い浄化率で処理することができる排気ガス浄化用触媒を加熱することにより、低温の排気ガスも高温の排気ガスと同様に高効率で浄化できるとともに、高い触媒機能と耐久性、信頼性に優れた排気ガス浄化装置を実現できる。

【００９２】請求項１７に記載の発明によれば、請求項１６における効果に加え、排気ガスフィルターをケースに収納し、ケースに排気ガスの流入・流出口を設けたことによって、ディーゼルエンジンの排気系に容易に取り付けることができる排気ガス浄化装置を実現できる。

【００９３】請求項１８に記載の発明によれば、請求項１７における効果に加え、ディーゼルエンジンの排気系における低温の排気ガスを加熱流体にして排気ガス浄化用触媒に吹き付けることにより、低温での排気ガスの浄化効率をも向上させることができる排気ガス浄化装置を実現できる。

【００９４】請求項１９に記載の発明によれば、被毒による触媒機能の低下が防止された排気ガス浄化用触媒を有した排気ガス浄化装置を用いているので、触媒機能に優れ、耐久性や信頼性に優れるとともに、排気ガスの温度低下が抑制されることにより、排気ガスの浄化効率を向上させた排気ガス浄化システムを実現できる。

【００９５】請求項２０に記載の発明によれば、請求項１９における効果に加え、排気ガスの温度低下を防止することにより、排気ガスの浄化効率を向上させた排気ガス浄化システムを実現できる。

【図面の簡単な説明】

【図１】本発明の実施の形態１における排気ガス浄化用触媒の製造方法の工程図

【図２】触媒活性評価試験に用いた固定床流通系反応装置の概略図

【図３】実施例１～９における排気ガス浄化用触媒の触媒活性評価試験の燃焼率の経時変化を示す図

【図４】比較例１～９における排気ガス浄化用触媒の触媒活性評価試験の燃焼率の経時変化を示す図

【図５】本発明は実施の形態２における排気ガス浄化用触媒フィルターの断面図

【図６】本発明の実施の形態３における排気ガス浄化装置の断面図

【図７】本発明の実施の形態４における排気ガス浄化装置の断面図

【図８】本発明の実施の形態５における排気ガス浄化装置の断面図

【図９】本発明の実施の形態６における排気ガス浄化装置の断面図

【図１０】本発明の実施の形態７における排気ガス浄化装置の断面図

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【符号の説明】

１　秤量工程
２　含浸工程
３　乾燥工程
４　焼成工程
５　耐熱性ハニカム構造物
６　多孔性無機物
７　触媒活性成分
８　ケース
９　排気ガス流入口
１０　排気ガス浄化用触媒
１１　排気ガス流出口
１２　ケース
１３　排気ガス流入口
１４　排気ガス浄化用触媒
１５　排気ガス流出口
１６　加熱手段
１７　送風手段
１８　ケース
１９　排気ガス流入口
２０　加熱手段
２１　排気ガス浄化用触媒
２２　排気ガス流出口
２３　エンジン
２４　マニホールド部
２５　送風手段
２６　ケース
２７　排気ガス流入口

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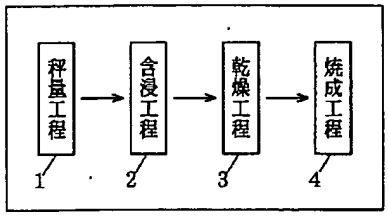
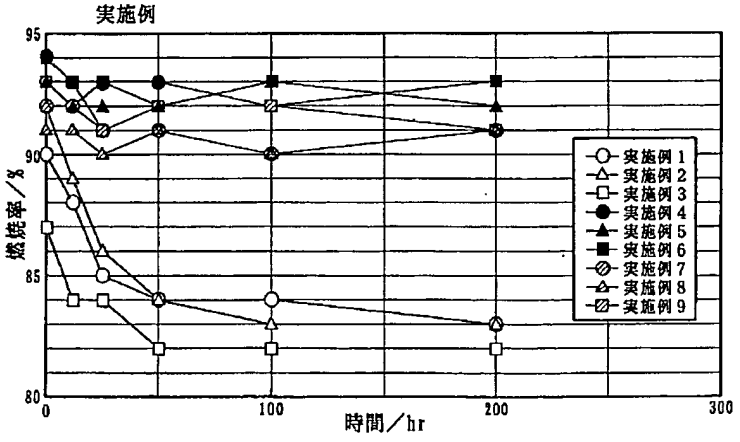
＊２８　加熱手段
２９　排気ガス浄化用触媒
３０　排気ガス流出口
３１　エンジン
３２　マニホールド部
３３　断熱材
３４　接続管
３５　送風手段
３６　ケース
３７　排気ガス流入口
３８　加熱手段
３９　排気ガス浄化用触媒
４０　排気ガス流出口
４１　窒素ガス
４２　乾燥空気
４３　ＳＯＦ
４４　気体用流量調整器
４５　気体用流量調整器
４６　液体用流量調整器
４７　気化器
４８　石英管
４９　排気ガス浄化用触媒
５０　石英ウール
５１　電気炉
５２　ＮＤＩＲ方式の一酸化炭素、二酸化炭素ガス分析計
５３　酸素センサ
＊

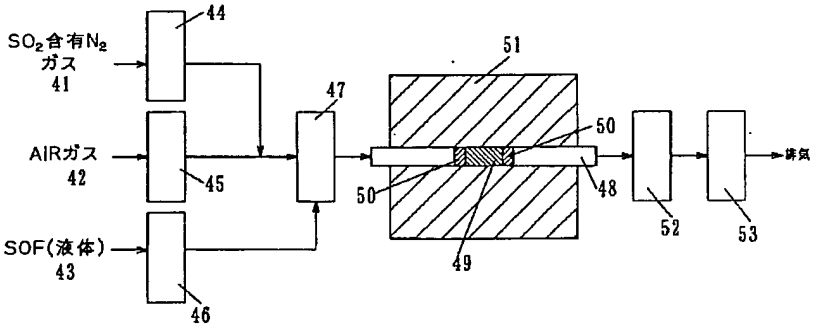
【図１】



【図３】

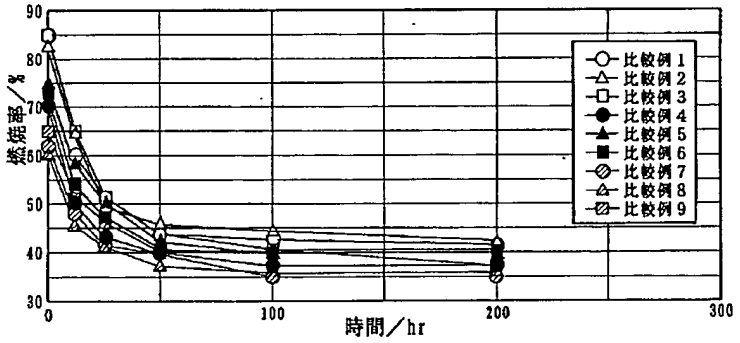


【図２】

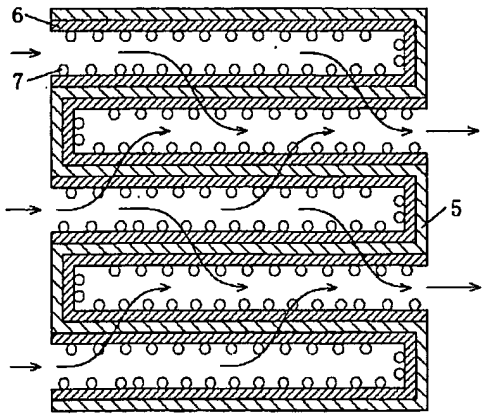

SO2含有N2
ガス
41
AIRガス
42
SOF(液体)
43
44
45
46
47
48
49
50
51
52
53
排気

【図４】

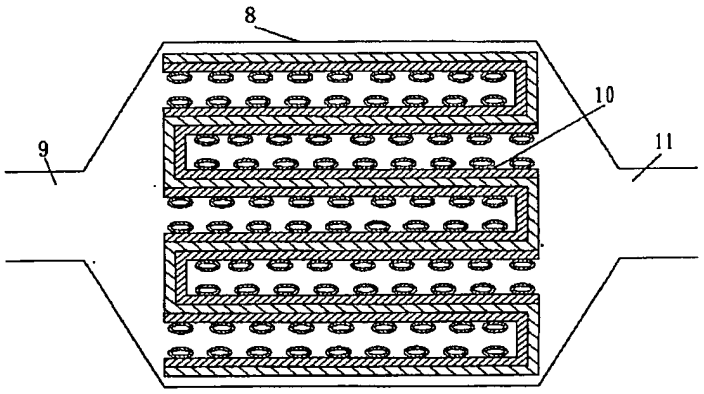
比較例


燃焼率／%
時間／hr
比較例１
比較例２
比較例３
比較例４
比較例５
比較例６
比較例７
比較例８
比較例９

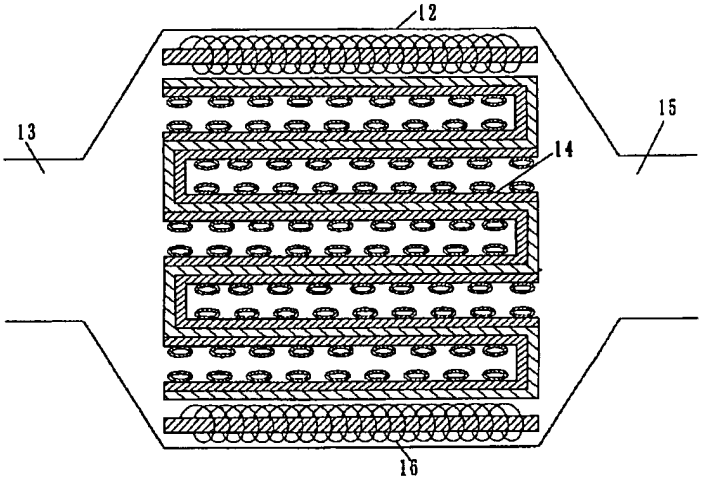
【図５】


6
7
5

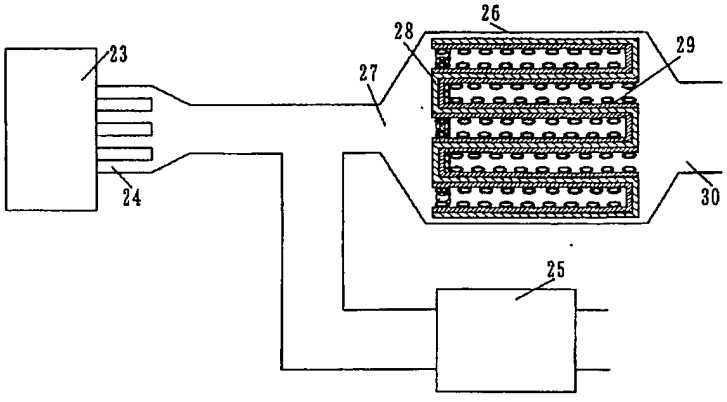
【図６】



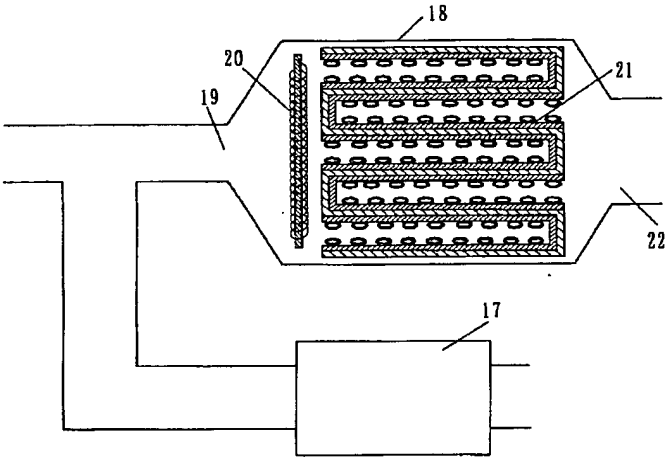
【図７】



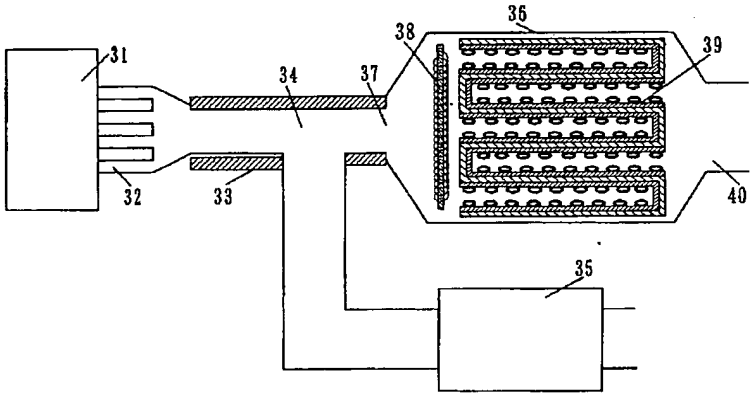
【図９】



【図８】



【図１０】



フロントページの続き

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(54) PRODUCTION OF CATALYST FOR PURIFYING EXHAUST GAS, EXHAUST GAS FILTER IN WHICH THE SAME IS USED, EXHAUST GAS PURIFICATION DEVICE AND EXHAUST GAS PURIFICATION SYSTEM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a producing method of a catalyst for purifying exhaust gas in which poisoning resistance for sulfur oxide is excellent by inhibiting reaction with sulfur oxide contained in exhaust gas of an internal combustion engine and to provide an exhaust gas filter, an exhaust gas purification device and an exhaust gas purification system.
SOLUTION: The method for producing a catalyst for purifying exhaust gas has the following processors. In a carrying process for impregnating and carrying a catalytic active ingredient on a catalytic carrier, a complexing agent of proper amount is added into a mixed solution in which the catalytic active ingredient and the carrier are mixed. The mixed solution is stirred and the catalytic carrier is dried and thereafter burned at the prescribed temperature in the reducing atmosphere and furthermore burned at the prescribed temperature in the oxidizing atmosphere containing sulfur oxide. The complexing agent contains sulfur in the constitutional ingredient of the molecule and forms a complex together with the catalytic ally active ingredient.

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1]It is a manufacturing method of a catalyst for exhaust gas purification characterized by comprising the following, A manufacturing method of a catalyst for exhaust gas purification, wherein a complexing agent which forms said catalytic activity ingredient and a complex in said catalytic activity ingredient which has the support process of supporting said catalytic activity ingredient in said carrier, and is used for it at said support process is added.
A carrier which consists of a porous inorganic substance.
A catalytic activity ingredient which consists of any one or more kinds in the precious metals, a base metal, and a metallic oxide which were supported on the surface of said carrier.

[Claim 2]A manufacturing method of the catalyst for exhaust gas purification according to claim 1, wherein said complexing agent contains sulfur as an atom configurated for said catalytic activity ingredient.
[Claim 3]A manufacturing method of the catalyst for exhaust gas purification according to claim 1 or 2, wherein said complexing agent is a salt of a diethyldithiocarbamic acid derivative.
[Claim 4]A manufacturing method of the catalyst for exhaust gas purification according to claim 3, wherein a salt of said diethyldithiocarbamic acid derivative is diethyl diethyldithiocarbamate ammonium.
[Claim 5]A manufacturing method of the catalyst for exhaust gas purification according to claim 1 to 4 with which a mole ratio (a/b) is characterized by 1-10, and being preferably adjusted to 3-5 by the addition a of said complexing agent to the addition b of a catalytic activity ingredient.
[Claim 6]A manufacturing method of a catalyst for exhaust gas purification of claims 1 thru/or 5 given [any 1] in inner with which said support process is characterized for the pH of a mixed solution of said catalytic activity ingredient, said carrier, and said complexing agent by 0.1-2.0, and being carried out by adjusting to 1.5-2 preferably.
[Claim 7]A manufacturing method of the catalyst for exhaust gas purification according to claim 6 using acid which does not contain chlorine as a pH adjuster for adjusting the pH of said mixed solution.
[Claim 8]A manufacturing method of a catalyst for exhaust gas purification of claims 1 thru/or 7 given [any 1] in inner with which a baking process which calcinates said carrier which supported said catalyst is characterized by having an oxidation baking process calcinated under an oxidizing atmosphere.
[Claim 9]A manufacturing method of the catalyst for exhaust gas purification according to claim 8 calcinating at a bottom of oxidizing atmosphere containing sulfur oxide gas predetermined temperature after said oxidation baking process calcinates at a temperature predetermined [in an oxidizing atmosphere].
[Claim 10]A manufacturing method of claim 8 or a catalyst for exhaust gas purification of 9 given [any 1] in inner with which it is characterized by calcinating at a predetermined temperature under an oxidizing atmosphere containing sulfur oxide gas and a steam after said oxidation baking process calcinates at a temperature predetermined [in an oxidizing atmosphere].
[Claim 11]A manufacturing method of a catalyst for exhaust gas purification of claims 8 thru/or 10 given [any 1] in inner with which calcination temperature under an oxidizing atmosphere containing the bottom of existence of sulfur oxide gas of said oxidation baking process or sulfur oxide gas, and a steam is characterized by 100-1000 ** of things preferably performed at 400-500 **.
[Claim 12]A manufacturing method of a catalyst for exhaust gas purification of claims 8 thru/or 11 given [any 1] in inner with which firing time under an oxidizing atmosphere containing the bottom of existence of sulfur oxide gas of said oxidation baking process or sulfur oxide gas, and a steam is characterized by being 20 to 30 hours preferably for 1 to 100 hours.

[Claim 13]A manufacturing method of a catalyst for exhaust gas purification of claims 1 thru/or 12 being the activated alumina in which said carrier coated silica given [any 1] in inner.
[Claim 14]A manufacturing method of the catalyst for exhaust gas purification according to claim 13, wherein in main particle diameter 50-200m^2/g has 0.4 cc/g - 1 cc/g in specific surface area of said activated alumina and 0.3-10 micrometers and pore volume have them.
[Claim 15]An exhaust gas filter comprising:
A honeycomb structured body made from ceramics which a main part is formed in cylindrical shape or a prismatic form, has many cells in shaft orientations, and was closed with encapsulant in either of the both-ends sides of each of said cell.
A catalyst for exhaust gas purification produced with a manufacturing method of a catalyst for exhaust gas purification of claims 1 thru/or 14 supported by cell wall of said honeycomb structured body given [any 1] in inner.

[Claim 16]An exhaust gas purifying facility comprising:
An exhaust gas filter indicated to claim 15.
A heating method which heats said exhaust gas filter.

[Claim 17]The exhaust gas purifying facility according to claim 16 provided with a case where it has an exhaust-gas-flow entrance which stored said exhaust gas filter and was formed in a one side part, and the exhaust emission outlet port formed in an other side portion.
[Claim 18]The exhaust gas purifying facility according to claim 17 having the blowing means allocated near said case.
[Claim 19]An exhaust gas cleaning system, wherein an exhaust gas purifying facility of claims 16 thru/or 18 given [any 1] in inner is allocated near the manifold part directly under an engine.
[Claim 20]The exhaust gas cleaning system according to claim 19 equipping a periphery of a communication trunk of said manifold part and an exhaust-gas-flow entrance of said case with thermal insulation.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]A manufacturing method of the catalyst for exhaust gas purification with which this invention purifies the exhaust gas of an internal-combustion engine, And the exhaust gas purifying facility using the catalyst for exhaust gas purification, especially the carbon monoxide contained in a Diesel engine exhaust gas, It is related with the exhaust gas filter, exhaust gas purifying facility, and exhaust gas cleaning system using a manufacturing method and the catalyst for exhaust gas purification of hydrocarbon and the catalyst for exhaust gas purification which carries out oxidation combustion of the particulate and purifies it.
[0002]
[Description of the Prior Art]It is desirable on environmental protection to carry out purifying treatment so that the exhaust gas from an internal-combustion engine may be emitted safely in the atmosphere. About the gasoline engine, the toxic substances in exhaust gas are decreasing in number certainly by a so-called appearance and further improvement of a three way component catalyst on progress of severe regulation of exhaust gas and the art over it, and a concrete target. By however, existence of the detrimental constituent called the unique principle and particulate about a diesel power plant. Development of the exhaust gas purifying facility using the catalyst for exhaust gas purification for which it is behind also in the technical development for toxic substance discharge control greatly that regulation is loose compared with a gasoline engine, and regulation is also loose compared with the gasoline engine, and the interval can purify it certainly, and the catalyst for exhaust gas purification is desired.
[0003]The open-type SOF (Soluble Organic Fraction; soluble organic component, hydrocarbon of high boiling point) decomposition catalyst which is the fundamentally same composition as a three way component catalyst as a catalyst which purifies the exhaust gas from the diesel power plant currently developed by the present is known. By the impregnating method which is publicly known art, in the prepared open-type SOF decomposition catalyst. For example, metal particles, such as a platinum metal which is a catalytic activity ingredient as well as a gasoline engine, distribute on the carrier of high specific surface area as indicated by JP,1-171626,A, It is supported, and with carbon monoxide and hydrocarbon, SOF in a diesel particulate carries out oxidative degradation, and is purified. The activated alumina etc. in which activated alumina or alkaline metals, and rare earth, such as gamma-alumina, were added in consideration of heat resistance etc. as a carrier of high specific surface area are used. Although there is a fault that this open-type SOF decomposition catalyst has a low extraction ratio of a dry suit, Since the quantity of a dry suit has the big merit that a regeneration device is unnecessary so that it is possible to decrease by a mechanical improvement of the diesel power plant itself or improvement of the fuel itself, improvement in much more future art is expected. However, catalytic activity falls with the catalyst poisoning substance in which an open-type SOF decomposition catalyst is also included in exhaust gas. Namely, for the gas oil used for a diesel power plant. Since 0.40 to 0.45% of the weight of sulfur content contains at present and about 0.05% of the weight of sulfur content contains after long-term regulation implementation, in the case of engine combustion, sulfur content oxidizes, it becomes a sulfur oxide, this acts with a catalytic activity ingredient, and catalytic activity falls.
[0004]Then, in order to raise fundamental catalytic activity, the method of preparing by the system which added multi-base carboxylic acid, such as citrate, etc. by the conventional impregnating method is indicated by JP,60-8863,B. Although the penetration depth from the surface of a catalyst component to an inside is controlled and catalytic activity is raised by supporting a catalytic activity ingredient on the outside surface of the carrier of the shape of a ball, or a pellet type, By the time it controls the particle

diameter and distribution state of the catalyst component itself, it will not result, therefore poisoning ****** by a sulfur oxide and catalytic activity fall temporally, and lack in endurance.

[0005]

[Problem(s) to be Solved by the Invention]as mentioned above, in the conventional catalyst for exhaust gas purification, since preventing an operation with a sulfur oxide effectively was not fully made, it was lacking in the poisoning-proof nature by a sulfur oxide, catalyst performance deteriorated temporally, and it had ****** that the life as a catalyst for cars was short.

[0006]By this invention's solving the above-mentioned conventional technical problem, and preventing an operation with the sulfur oxide and the catalyst for exhaust gas purification which are included in an internal-combustion engine, especially the exhaust gas from a diesel power plant, Offer of the manufacturing method of the catalyst for exhaust gas purification excellent in the poisoning-proof nature to a sulfur oxide, And offer of the exhaust gas filter which was excellent in reliability or endurance while excelling in the poisoning-proof nature to a sulfur oxide, And it aims at offer of the exhaust gas purifying facility which was excellent in reliability or endurance by high purification nature, and offer of the exhaust gas cleaning system which caught SOF etc. with high collection efficiency and was excellent in reliability or endurance.

[0007]

[Means for Solving the Problem]In order to solve said technical problem, a manufacturing method of a catalyst for exhaust gas purification of this invention, In a support process of carrying out impregnating support of the catalytic activity ingredient on catalyst support, in a mixed solution which mixed a carrier with a catalytic activity ingredient, A proper quantity of complexing agents which contain sulfur in a constituent of a molecule and which form a catalytic activity ingredient and a complex are added, and said mixed solution is calcinated at a predetermined temperature after stirring and desiccation and among reducing atmosphere, and also it calcinates at a predetermined temperature among an oxidizing atmosphere. It has desirably the composition calcinated at a predetermined temperature further among an oxidizing atmosphere containing a sulfur oxide. Carbon monoxide contained in exhaust gas from a diesel power plant by this, When carrying out oxidation combustion of the SOF in hydrocarbon and a particulate and purifying it, A manufacturing method of a catalyst for exhaust gas purification which can mass-produce a long lasting catalyst for exhaust gas purification by low cost which it became possible to prevent an operation with a sulfur oxide and a catalytic activity ingredient which are catalyst poison, and was excellent in poisoning-proof nature to a sulfur oxide is realizable.

[0008]An exhaust gas filter of this invention has the composition provided with said catalyst for exhaust gas purification supported by each cell wall of a honeycomb structured body made from ceramics. An exhaust gas filter which was excellent in poisoning-proof nature to a sulfur compound in exhaust gas, maintained high catalytic activity for a long period of time, and was excellent in reliability or endurance by this is realizable.

[0009]An exhaust gas purifying facility of this invention consists of composition which equipped a manufacturing method of a catalyst for exhaust gas purification of this invention with a case for storing a heat-resistant honeycomb structured body for supporting a catalyst which carried out ****** production, and said catalyst, and a heat-resistant honeycomb structured body with a catalyst. Carbon monoxide contained in exhaust gas from a diesel power plant by these composition, When carrying out oxidation combustion of the SOF in hydrocarbon and a particulate and purifying it, it becomes possible to prevent an operation with a sulfur oxide and a catalytic activity ingredient which are catalyst poison, and an exhaust gas purifying facility which was excellent in poisoning-proof nature to a sulfur oxide, and was excellent in endurance can be provided.

[0010]An exhaust gas cleaning system of this invention has the composition which allocated said exhaust gas purifying facility near the manifold part directly under a diesel power plant. While being able to purify by this exhaust gas having contained high-concentration SOF etc. by a high purifying rate, an exhaust gas cleaning system which maintained high catalytic activity for a long period of time, and was excellent in reliability or endurance is realizable.

[0011]

[Embodiment of the Invention]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 1, The catalytic activity ingredient which consists of any one or more kinds in the precious metals, base metal, and metallic oxide which were supported on the surface of the carrier which consists of a porous inorganic substance, and said carrier, It is a manufacturing method of the catalyst for exhaust gas purification which ****, and it has the support process of supporting said catalytic activity ingredient to said carrier, and has the composition by which the complexing agent which forms said

catalytic activity ingredient and a complex in said catalytic activity ingredient used at said support process is added. By this composition, atomization and high decentralization of a catalytic activity ingredient are attained, and the surface area of the catalyst which contributes to a reaction becomes remarkably large, and it has the operation that activity improves.

[0012]Here, as a porous inorganic substance, it has high specific surface area and porous bodies, such as alpha-alumina, silica, silica alumina, a titania, magnesia, and zirconia, can also be used besides activated alumina. The porous mineral matter which coated the surface of the porous inorganic substance with other oxide films may be used. As a method of forming an oxide film, after covering with the impregnating method, dip coating, etc. to a carrier surface, it dries and the method of calcinating, etc. are used, but the starting material of said oxide can use the alkoxide of each metal, each metal salt, etc.

[0013]As a catalytic activity ingredient, platinum, palladium, rhodium, osmium, The precious metals, such as iridium, a ruthenium, gold, and silver, lithium, sodium, Potassium, a rubidium, caesium, magnesium, calcium, strontium, Barium, a scandium, yttrium, titanium, a zirconium, hafnium, Vanadium, niobium, tantalum, chromium, molybdenum, tungsten, Manganese, technetium, a rhenium, iron, cobalt, nickel, copper, Base metals, such as zinc and tin, copper oxide, nickel oxide, cobalt oxide, a lanthanum trioxide, Cerium oxide, iron oxide, vanadium oxide, a zinc oxide, chrome oxide, an aluminum oxide, A calcium oxide, barium oxide, gold oxide, silver oxide, platinum oxide, oxidation palladium, Thallium oxide, thorium oxide, titanium oxide, oxidized silicon, magnesium oxide, Metallic oxides, such as molybdenum oxide, yttrium oxide, zirconium oxide, and beryllium oxide, ABO_3 (A -- at least one or more kinds of elements of rare earth, such as a lantern and cerium, and B -- alkaline-earth metals, such as alkaline metals, such as transition metals, such as chromium, manganese, iron, and cobalt, lithium, and sodium, strontium, and barium, and platinum.) Any one or more kinds in metal multiple oxides, such as a perovskite type multiple oxide which makes basic structure at least one or more kinds of elements in the precious metals, such as palladium, a spinel type multiple oxide, and a perovskite spinel multiple oxide, are used.

[0014]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 2 has the composition whose complexing agent which forms a catalytic activity ingredient and a complex contains sulfur as an atom configurated for a catalytic activity ingredient in claim 1. The metal complex where physical properties were stabilized more by configurating with a sulfur atom by this composition is formed, From the atomic radius of sulfur used as a ligand being larger than the atomic radius of the ligand of other complexing agents. It has the operation that can form a more nearly three-dimensional metal complex, the distance between metal ions becomes uniform in three dimensions as a result, and the dispersibility of the catalytic activity ingredient in a carrier surface becomes uniform.

[0015]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 3 has the composition which the complexing agent which forms a catalytic activity ingredient and a complex becomes from the salt of a diethyldithiocarbamic acid derivative in claim 1 or 2. By this composition, a catalytic activity ingredient forms two sulfur atoms and complexes which are contained in the salt of a diethyldithiocarbamic acid derivative, Under the present circumstances, it has the operation of being supported by high distribution with a fixed distance which exists when a sulphuric atomic radius forms a three-dimensional complex from a large thing and is supported by the carrier surface.

[0016]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 4 has the composition whose salt of said diethyldithiocarbamic acid derivative is diethyl diethyldithiocarbamate ammonium in claim 3. By this composition, two sulfur atoms and complexes which are contained in diethyl diethyldithiocarbamate ammonium are formed, Under the present circumstances, while supporting to high distribution with a fixed distance which exists when a sulphuric atomic radius forms a three-dimensional complex from a large thing and is supported by the carrier surface, it has the operation that the complex stable with two diethyl ammonium is formed.

[0017]In the addition a of said complexing agent, in the inside [manufacturing method / of the catalyst for exhaust gas purification of this invention according to claim 5] 1 [any] of claims 1 thru/or 4, the mole ratio (a/b) has 1-10, and the composition preferably adjusted to 3-5 to the addition b of a catalytic activity ingredient. By this composition, it has the operation that a metal complex is formed efficiently.

[0018]Are based also on the kind of catalytic activity ingredient here as a mole ratio (a/b) becomes smaller than 3, but. Are based also on the kind of catalytic activity ingredient as formation of a metal complex is insufficient, the tendency for the dispersibility of a catalytic activity ingredient to become uneven is accepted and especially a mole ratio (a/b) becomes larger than 5 remarkably [this tendency] less than one in a mole ratio (a/b), but. Since this tendency will become remarkable if what does not participate in uniform distribution increases, the tendency for most catalytic activity to reach a balance is accepted and

especially a mole ratio (a/b) exceeds 10, neither is preferred.
[0019]In the inside [manufacturing method / of the catalyst for exhaust gas purification of this invention according to claim 6] 1 [any] of claims 1 thru/or 5, said support process has 0.1-2.0, and the composition performed by adjusting to 1.5-2 preferably for the pH of the mixed solution of a catalytic activity ingredient, a carrier, and a complexing agent. By this composition, the solubility of metal salt of the catalytic activity ingredient in a mixed solution improves, complexing of a complexing agent becomes easy, and it has the operation that the uniform dispersibility of a catalytic activity ingredient when it is considered as a catalyst improves.
[0020]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 7 has the composition using the acid which does not contain chlorine as a pH adjuster for adjusting the pH of said mixed solution in claim 6. By this composition, residual chlorine is kept from remaining into a catalyst, and it has the operation which controls the poisoning by chlorine.
[0021]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 8 is provided with the composition in which the baking process which calcinates the carrier which supported the catalyst to the inside 1 [any] of claims 1 thru/or 7 has an oxidation baking process calcinated under an oxidizing atmosphere. Thereby, reduction firing supports a catalyst component with a metaled form on a carrier, and it has the operation that the heat resistance under an oxidizing atmosphere is securable by making oxygen contact by oxidation calcination.
[0022]It is preferred to establish the reduction firing process of calcinating the carrier which supported the catalyst under reducing atmosphere as a previous process of an oxidation baking process. A catalyst component is supported with a metallic state by reduction firing on a carrier.
[0023]In claim 8, the manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 9 has the composition which calcinates at a bottom of oxidizing atmosphere containing sulfur oxide gas predetermined temperature, after said oxidation baking process calcinates at a temperature predetermined [in an oxidizing atmosphere]. It has the operation whose ingredient [inertness / oxidation reaction / of the catalytic activity ingredients] is changed to an ingredient [activity / oxidation reaction] by this. Here, 10-10000 ppm is used as concentration of sulfur oxide gas. Although sulfur oxide gas is enough if equivalent introduction is carried out with a catalytic activity ingredient, and decided in "temperature x time", the inside of a mentioned range is used suitably.
[0024]In claim 8 or 9, the manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 10 has the composition which calcinates at a predetermined temperature under the oxidizing atmosphere containing sulfur oxide gas and a steam, after said oxidation baking process calcinates at a temperature predetermined [in an oxidizing atmosphere]. This has the operation of removing the remains ingredient of the salt of a catalyst component. It has the operation of preventing poisoning of the catalytic activity ingredient being carried out by this. It has the operation whose thing which was inertness is changed to a thing [activity / oxidation reaction] in the oxidation reaction of the catalytic activity ingredients. Here, 1 - 50vol% is used as concentration of a steam. The steam concentration of this range removes the remains ingredient in a system effectively, poisoning by the remains ingredient of a catalytic activity ingredient is prevented, and it has the operation of giving expected catalytic activity.
[0025]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 11, In claims 8 thru/or 10, the calcination temperature under the oxidizing atmosphere containing the bottom of existence of the sulfur oxide gas of said oxidation baking process or sulfur oxide gas, and a steam has 100-1000 ** of composition preferably performed at 400-500 **. It has the operation which changes by this what was inertness to the oxidation reaction of the catalytic activity ingredients at a thing [activity / oxidation reaction].
[0026]Here what was inertness to the oxidation reaction of the catalytic activity ingredients as calcination temperature becomes lower than 400 degreeC, Since the tendency which becomes is hard to be acquired in the effect of making it change to a thing [activity / oxidation reaction] is accepted, and the tendency for sulfur oxide gas to be unable to perform a catalyst component and a reaction stably, but for catalytic activity to turn into inertness is accepted as it becomes higher than 500 **, neither is preferred.
[0027]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 12, claims 8 thru/or 11 -- inner -- in any 1, the firing time under the oxidizing atmosphere containing the bottom of existence of the sulfur oxide gas of said oxidation baking process or sulfur oxide gas, and a steam has the composition which is 20 to 30 hours preferably for 1 to 100 hours. It has the operation which changes by this what was inertness to the oxidation reaction of the catalytic activity ingredients at a thing [activity / oxidation reaction].

[0028]Since the tendency for expected catalytic activity to be hard to be acquired is accepted here as firing time becomes shorter than 20 hours, and the tendency for catalytic activity to reach a balance is accepted as it becomes longer than 30 hours, neither is preferred.
[0029]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 13 has the composition which is the activated alumina in which said carrier coated the inside 1 [any] of claims 1 thru/or 12 with silica. Also when this heat-treats in the oxidizing atmosphere containing sulfur oxide gas, the reaction of a carrier and a sulfur oxide is inhibited and it has the operation that the fall of the specific surface area accompanying processing can be prevented.
[0030]The manufacturing method of the catalyst for exhaust gas purification of this invention according to claim 14 has the composition whose 0.3-10 micrometers and pore volume in main particle diameter 50-200m^2/g has 0.4 cc/g-1cc/g in the specific surface area of said activated alumina, and have it in claim 13. By this, a catalytic activity ingredient distributes uniformly, and it can support with the state where it microatomized, and has the operation that large surface area can be obtained.
[0031]The honeycomb structured body made from ceramics which a main part is formed in cylindrical shape or a prismatic form, and the invention of this invention according to claim 15 has many cells in shaft orientations, and was closed with encapsulant in either of the both-ends sides of each of said cell, It has the composition provided with the catalyst for exhaust gas purification produced with the manufacturing method of the catalyst for exhaust gas purification of claims 1 thru/or 14 supported by the cell wall of said honeycomb structured body given [any 1] in inner. Since the carrier which distributed uniformly the catalytic activity ingredient excellent in poisoning-proof nature by this is supported to the cell wall, while it can be efficient, being able to decompose and being able to purify SOF in exhaust gas, etc., it has the operation that endurance and reliability can be improved.
[0032]The invention of this invention according to claim 16 has the composition which has the exhaust gas filter indicated to claim 15, and a heating method which heats said exhaust gas filter. By this heating the catalyst for exhaust gas purification, it has the operation that low-temperature exhaust gas as well as hot exhaust gas is efficient, and can be purified.
[0033]An electric heater, a burner, microwave, etc. are used as a heating method. The invention of this invention according to claim 17 has the composition provided with the case where it has the exhaust-gas-flow entrance which stored said exhaust gas filter and was formed in the one side part, and the exhaust emission outlet port formed in the other side portion, in the invention according to claim 16.
[0034]It has the operation that it can attach to the exhaust system of a diesel power plant, by having stored the catalyst for exhaust gas purification in the case, and having established the inflow and the tap hole of exhaust gas in the case by this.
[0035]Metal, ceramics, etc. which were excellent in oxidation resistance as a case are used. The invention of this invention according to claim 18 has the composition which has the blowing means allocated near said case in the invention according to claim 17. It has the operation that the purification efficiency of low-temperature exhaust gas improves, by using the exhaust gas of the low temperature in the exhaust system of a diesel power plant as heating fluid, and spraying the catalyst for exhaust gas purification by this.
[0036]A blower, a compressor, etc. are used as a blowing means. The invention of this invention according to claim 19 has the composition allocated near the manifold part directly under an engine in the exhaust gas purifying facility of claims 16 thru/or 18 given [any 1] in inner. This has the operation that the purification efficiency of exhaust gas improves, by controlling the temperature fall of exhaust gas.
[0037]The invention of this invention according to claim 20 has the composition which equipped the periphery of the communication trunk of said manifold part and the exhaust-gas-flow entrance of said case with thermal insulation in claim 19. This has the operation that the purification efficiency of exhaust gas improves, by preventing the temperature fall of exhaust gas.
[0038]The metal etc. which were excellent in oxidation resistance as a communication trunk are used, and asbestos, glass wool, slag wool, etc. are used as thermal insulation.
[0039]Hereafter, the example of an embodiment of the invention is explained using a drawing.
(Embodiment 1) Drawing 1 is process drawing of the manufacturing method of the catalyst for exhaust gas purification in the embodiment of the invention 1. The manufacturing process of the manufacturing method of the catalyst for exhaust gas purification in Embodiment 1 consists of four processes, the weighing process 1, the impregnation process 2, the drying process 3, and the baking process 4. In the impregnation process 2, while mixing with a catalytic activity ingredient the complexing agent which forms a complex, a carrier is impregnated. In the baking process 4, it calcinates by reducing atmosphere first and then calcinates by an oxidizing atmosphere. It calcinates in the oxidizing atmosphere which contained the

specific component further if needed.
[0040]It explains in more detail based on an example below.
[0041]
[Example]
(Example 1)
Adding the 10wt section and carrying out stirring mixing of the tetraethoxysilane (made by Kanto Kagaku) as it is one whole day and night, ethanol was evaporated in the ethanol solution 100wt section of <preparation of carrier> activated alumina powder (made by Sumitomo Chemical), and it was made to harden by drying. After making a lump into powder state with a mortar, the carrier which calcinates at 800 ** for 5 hours, and consists of silica-coding activated alumina was obtained.
[0042]The palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the <preparation of solution of catalytic activity ingredient> concentration 97-102, The dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the diethyl diethyldithiocarbamate ammonium (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section were mixed, and the solution of the catalytic activity ingredient was obtained.
[0043]The silica-coding activated alumina powder <manufacture of an exhaust gas filter> Obtained The 10wt section, Mix the 1wt section for an aluminium nitrate (made by Wako Pure Chemical Industries), mix the 5wt section and the distilled water 100wt section for alumina sol (product made from the Nissan chemicals), and in the obtained slurry The honeycomb filter made from cordierite. It pulls up, after (for example, the product made from NGK) is immersed for 1 minute, and after blowing off an excessive slurry by a blowing air etc., it dries at 120 ** for 2 hours. Subsequently, it calcinated at 800 ** for 5 hours, and silica-coding activated alumina was supported on the surface of the honeycomb filter made from mullite. Next, it pulls up, after the obtained honeycomb filter is immersed in the solution of the catalytic activity ingredient neglected after preparation one whole day and night for 10 minutes, and after blowing off an excessive solution by a blowing air etc., it dries at 120 ** for 2 hours. Subsequently, after calcinating in 2-hour reducing atmosphere at 600 **, the catalytic activity ingredient which calcinates in a 5-hour oxidizing atmosphere at 800 **, and also calcinates in a 5-hour oxidizing atmosphere at 450 **, and consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.
[0044](Example 2) After stirring the silica-coding activated alumina obtained in Example 1 one whole day and night after mixing the 100wt section and the solution 100wt section of the catalytic activity ingredient obtained in Example 1, the 10wt section is added to this mixed solution, and a thickener is mixed to it. To this mixed solution, subsequently, the honeycomb filter made from cordierite. After pulling up after (for example, the product made from NGK) is immersed for 10 minutes, and blowing off an excessive solution by a blowing air etc., after drying at 120 ** for 2 hours, calcinate at 600 ** for 2 hours, and also it calcinates in a 5-hour oxidizing atmosphere at 800 **, The catalytic activity ingredient which calcinates in a 5-hour oxidizing atmosphere at 450 more **, and consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.
[0045](Example 3) The silica-coding activated alumina obtained in Example 1 The 100wt section, After stirring one whole day and night after mixing the solution 100wt section of the catalytic activity ingredient obtained in Example 1, After adding the 10wt section to this mixed solution and stirring a thickener after mixing to it one whole day and night, after drying at 120 ** for 2 hours, it calcinated at 600 ** for 2 hours, and the catalytic activity ingredient was supported on the carrier, and it was considered as the catalyst for exhaust gas purification. To next, the slurry which mixed and prepared said catalyst 100wt section for exhaust gas purification, the thickener 10wt section, and the distilled water 200wt section. The honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 10 minutes, Subsequently, after blowing off an excessive solution by a blowing air etc. and drying at 120 ** for 2 hours, calcinate said honeycomb filter in a 5-hour oxidizing atmosphere at 800 **, and it ranks second, The exhaust gas filter which coated the carrier which calcinated in a 5-hour oxidizing atmosphere at 450 more **, and supported the catalyst on the surface of said honeycomb filter was obtained.
[0046](Example 4) The silica-coding activated alumina obtained in Example 1 The 10wt section, In the slurry produced by mixing the 1wt section for an aluminium nitrate (made by Wako Pure Chemical Industries), and mixing the 5wt section and the distilled water 100wt section for alumina sol (product made from the Nissan chemicals), It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 1 minute, After blowing off an excessive slurry by a blowing air etc. and drying at 120 ** for 2 hours, said honeycomb filter was calcinated at 800 ** for 5 hours, and the honeycomb filter made from mullite which supported silica-coding activated alumina on the surface was

produced. Next, after the honeycomb filter obtained after neglecting it one whole day and night in the solution 100wt section of the catalytic activity ingredient obtained in Example 1 is immersed in the solution of this catalytic activity ingredient for 10 minutes, it is pulled up, and after blowing off an excessive solution by a blowing air etc., it dries at 120 ** for 2 hours. Subsequently, after calcinating in 2-hour reducing atmosphere at 600 **, calcinate in a 5-hour oxidizing atmosphere at 800 **, and also said honeycomb filter is calcinated in the oxidizing atmosphere containing a sulfur oxide, The catalytic activity ingredient which consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.

[0047](Example 5) The silica-coding activated alumina obtained in Example 1 The 100wt section, After agitating the mixed water solution which mixed and obtained the solution 100wt section of the catalytic activity ingredient obtained in Example 1 one whole day and night, The honeycomb filter made from cordierite after carrying out the 10wt section addition of the thickener at this mixed water solution. After pulling up after (for example, the product made from NGK) is immersed for 10 minutes, and blowing off an excessive solution by a blowing air etc., After drying at 120 ** for 2 hours, calcinate among reducing atmosphere at 600 ** for 2 hours, and also calcinate in a 5-hour oxidizing atmosphere at 800 **, and also said honeycomb filter is calcinated at 450 ** among the oxidizing atmosphere containing a sulfur oxide, The catalytic activity ingredient which consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.

[0048](Example 6) The silica-coding activated alumina obtained in Example 1 The 100wt section, After mixing the solution 100wt section of the catalytic activity ingredient obtained in Example 1, it stirred one whole day and night, after drying at 120 ** subsequently for 2 hours, it calcinated at 600 ** for 2 hours, and the catalytic activity ingredient was supported on the carrier, and it was considered as the catalyst. To next, the slurry which mixed said catalyst 100wt section, the thickener 10wt section, and the distilled water 200wt section, and was prepared to predetermined viscosity. It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 10 minutes, After blowing off an excessive solution by a blowing air etc., drying at 120 ** for 2 hours and calcinating in a 5-hour oxidizing atmosphere at 800 more **, it calcinates at 450 ** among the oxidizing atmosphere containing 1000 ppm of sulfur oxides, The exhaust gas filter which coated the surface of said honeycomb filter with the carrier which supported the catalyst was obtained.

[0049](Example 7) The silica-coding activated alumina obtained in Example 1 The 10wt section, In the slurry produced by mixing the 1wt section for an aluminium nitrate (made by Wako Pure Chemical Industries), and mixing the 5wt section and the distilled water 100wt section for alumina sol (product made from the Nissan chemicals), It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 1 minute, After blowing off an excessive slurry by a blowing air etc., after drying at 120 ** for 2 hours, it calcinated at 800 ** for 5 hours, and silica-coding activated alumina was supported on the surface of the honeycomb filter made from mullite. Next, it pulls up, after the honeycomb filter obtained by the solution of this catalytic activity ingredient after neglecting the solution 100wt section of the catalytic activity ingredient obtained in Example 1 one whole day and night is immersed for 10 minutes, and after blowing off an excessive solution by a blowing air etc., it dries at 120 ** for 2 hours. Subsequently, after calcinating said honeycomb filter in 2-hour reducing atmosphere at 600 **, calcinate in a 5-hour oxidizing atmosphere at 800 **, and also it calcinates in the oxidizing atmosphere containing 1000 ppm of sulfur oxide, and steam 10vol%, The catalytic activity ingredient which consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.

[0050](Example 8) The silica-coding activated alumina obtained in Example 1 The 100wt section, After mixing the solution 100wt section of the catalytic activity ingredient obtained in Example 1, The honeycomb filter made from cordierite after stirring one whole day and night and adding the thickener of the 10wt section to this mixed solution. After pulling up after (for example, the product made from NGK) is immersed for 10 minutes, and blowing off an excessive solution by a blowing air etc., After drying at 120 ** for 2 hours, it calcinates among reducing atmosphere at 600 ** for 2 hours, After calcinating said honeycomb filter in a 5-hour oxidizing atmosphere at 800 **, it calcinates at 450 ** among the oxidizing atmosphere containing 1000 ppm of sulfur oxide, and steam 10vol%, The catalytic activity ingredient which becomes the upper surface of a carrier from the oxide of palladium, platinum, and these metal was made to support, and the exhaust gas filter was obtained.

[0051](Example 9) The silica-coding activated alumina obtained in Example 1 The 100wt section, After mixing the solution 100wt section of the catalytic activity ingredient obtained in Example 1, it stirred one whole day and night, after drying at 120 ** subsequently for 2 hours, it calcinated at 600 ** for 2 hours,

and the catalytic activity ingredient was supported on the carrier, and it was considered as the catalyst. To next, the slurry which mixed said catalyst, a thickener, and distilled water, and was prepared to predetermined viscosity. It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 10 minutes, After blowing off an excessive solution by a blowing air etc., drying at 120 ** for 2 hours and calcinating said honeycomb filter in a 5-hour oxidizing atmosphere at 800 ** further, It calcinated at 450 ** among the oxidizing atmosphere containing 1000 ppm of sulfur oxide, and steam 10vol%, and the exhaust gas filter which coated the carrier which supported the catalyst on the surface of said honeycomb filter was obtained.

[0052](Comparative example 1) The silica-coding activated alumina obtained in Example 1 The 10wt section, In the slurry produced by mixing the 1wt section for an aluminium nitrate (made by Wako Pure Chemical Industries), and mixing the 5wt section and the distilled water 100wt section for alumina sol (product made from the Nissan chemicals), It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 1 minute, After blowing off an excessive slurry by a blowing air etc., after drying at 120 ** for 2 hours, it calcinated at 800 ** for 5 hours, and silica-coding activated alumina was supported on the surface of the honeycomb filter made from mullite. Next, the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the citrate (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, It pulls up, after said honeycomb filter is immersed in the mixed water solution neglected one whole day and night for 10 minutes, After blowing off an excessive solution by a blowing air etc., after drying at 120 ** for 2 hours, calcinate among 2-hour reducing atmosphere at 600 **, and also it calcinates in a 5-hour oxidizing atmosphere at 800 **, The catalytic activity ingredient which calcinates in a 5-hour oxidizing atmosphere at 450 more **, and becomes the upper surface of said honeycomb filter from the oxide of palladium, platinum, and these metal was made to support, and the exhaust gas filter was obtained.

[0053](Comparative example 2) The silica-coding activated alumina obtained in Example 1 The 10wt section and the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the citrate (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, The honeycomb filter made from cordierite after stirring one whole day and night and adding the thickener of the 10wt section to this mixed solution. After pulling up after (for example, the product made from NGK) is immersed for 10 minutes, and blowing off an excessive solution by a blowing air etc., after drying at 120 ** for 2 hours, calcinate at 600 ** for 2 hours, and also it calcinates in a 5-hour oxidizing atmosphere at 800 **, The catalytic activity ingredient which calcinates in a 5-hour oxidizing atmosphere at 450 more **, and becomes the upper surface of said honeycomb filter from the oxide of palladium, platinum, and these metal was made to support, and the exhaust gas filter was obtained.

[0054](Comparative example 3) The silica-coding activated alumina obtained in Example 1 The 10wt section and the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the citrate (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, it stirred one whole day and night, after drying at 120 ** subsequently for 2 hours, it calcinated at 600 ** for 2 hours, and the catalytic activity ingredient was supported on the carrier, and it was considered as the catalyst. To next, the slurry which mixed said catalyst 100wt section, the thickener 10wt section, and the distilled water 200wt section, and was prepared to predetermined viscosity. It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 10 minutes, After blowing off an excessive solution by a blowing air etc., after drying at 120 ** for 2 hours, it calcinated in a 5-hour oxidizing atmosphere at 800 more **, and the carrier which supported the catalyst on the surface of said honeycomb filter was coated, and the exhaust gas filter was obtained.

[0055](Comparative example 4) The silica-coding activated alumina obtained in Example 1 The 10wt section, In the slurry produced by mixing the 1wt section for an aluminium nitrate (made by Wako Pure Chemical Industries), and mixing the 5wt section and the distilled water 100wt section for alumina sol (product made from the Nissan chemicals), It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 1 minute, After blowing off an excessive slurry by a blowing air etc., after drying at 120 ** for 2 hours, it calcinated at 800 ** for 5 hours, and the carrier which supported silica-coding activated alumina on the surface of the honeycomb filter made from mullite was produced. Next, the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the

concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the citrate (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, It pulls up, after a carrier is immersed in the mixed water solution neglected one whole day and night for 10 minutes, After blowing off an excessive solution by a blowing air etc., and drying at 120 ** for 2 hours, it calcinates among 2-hour reducing atmosphere at 600 **, Calcinated in a 5-hour oxidizing atmosphere at 800 more **, and also calcinated said honeycomb filter in the oxidizing atmosphere containing a sulfur oxide, the catalytic activity ingredient which consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.

[0056](Comparative example 5) The silica-coding activated alumina obtained in Example 1 The 10wt section and the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the citrate (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, The honeycomb filter made from cordierite after stirring one whole day and night and adding the thickener of the specified quantity to this mixed solution. After pulling up after (for example, the product made from NGK) is immersed for 10 minutes, and blowing off an excessive solution by a blowing air etc., After drying at 120 ** for 2 hours, calcinate at 600 ** for 2 hours, and also calcinate in a 5-hour oxidizing atmosphere at 800 **, and also said honeycomb filter is calcinated at 450 ** among the oxidizing atmosphere containing a sulfur oxide, The catalytic activity ingredient which consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.

[0057](Comparative example 6) The silica-coding activated alumina obtained in Example 1 The 10wt section and the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the diethyl diethyldithiocarbamate ammonium (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, It stirred one whole day and night, after drying at 120 ** subsequently for 2 hours, it calcinated at 600 ** for 2 hours, and the catalytic activity ingredient was supported on the carrier, and it was considered as the catalyst. To next, the slurry which mixed said catalyst, a thickener, and distilled water, and was prepared to predetermined viscosity. It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 10 minutes, After blowing off an excessive solution by a blowing air etc., after drying at 120 ** for 2 hours, calcinate in a 5-hour oxidizing atmosphere at 800 more **, and also said honeycomb filter is calcinated at 450 ** among the oxidizing atmosphere containing a sulfur oxide, The exhaust gas filter which coated the surface of said honeycomb filter with the carrier which supported the catalyst was obtained.

[0058](Comparative example 7) The silica-coding activated alumina obtained in Example 1 The 10wt section, In the slurry produced by mixing the 1wt section for an aluminium nitrate (made by Wako Pure Chemical Industries), and mixing the 5wt section and the distilled water 100wt section for alumina sol (product made from the Nissan chemicals), It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 1 minute, After blowing off an excessive slurry by a blowing air etc., after drying at 120 ** for 2 hours, it calcinated at 800 ** for 5 hours, and silica-coding activated alumina was supported on the surface of the honeycomb filter made from mullite. Next, the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the citrate (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, It pulls up, after said honeycomb filter is immersed in the mixed water solution neglected one whole day and night for 10 minutes, After blowing off an excessive solution by a blowing air etc., and drying at 120 ** for 2 hours, it calcinates among 2-hour reducing atmosphere at 600 **, Calcinated in a 5-hour oxidizing atmosphere at 800 more **, and also calcinated said honeycomb filter in the oxidizing atmosphere containing a sulfur oxide and a steam, the catalytic activity ingredient which consists of an oxide of palladium, platinum, and these metal on the surface of a carrier was made to support, and the exhaust gas filter was obtained.

[0059](Comparative example 8) The silica-coding activated alumina obtained in Example 1 The 10wt section and the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the citrate (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, The honeycomb filter made from cordierite after stirring one whole day and night and adding the thickener 10wt section to this mixed solution. After pulling up after (for example, the

product made from NGK) is immersed for 10 minutes, and blowing off an excessive solution by a blowing air etc., After drying at 120 ** for 2 hours, calcinate at 600 ** for 2 hours, and also it calcinates in a 5-hour oxidizing atmosphere at 800 **, Calcinated said honeycomb filter at 450 ** among the oxidizing atmosphere containing 1000 ppm of sulfur oxide, and steam 10vol%, the catalytic activity ingredient which becomes the upper surface of a carrier from the oxide of palladium, platinum, and these metal was made to support, and the exhaust gas filter was obtained.

[0060](Comparative example 9) The silica-coding activated alumina obtained in Example 1 The 10wt section and the palladium nitrate (made by Wako Pure Chemical Industries) 0.11wt section of the concentration 97-102, After mixing the dinitrodiaminoplatinum (product made from the Tanaka precious metals) 0.12wt section, the diethyl diethyldithiocarbamate ammonium (made by Wako Pure Chemical Industries) 0.70wt section, and the distilled water 100wt section, It stirred one whole day and night, after drying at 120 ** subsequently for 2 hours, it calcinated at 600 ** for 2 hours, and the catalytic activity ingredient was supported on the carrier, and it was considered as the catalyst. To next, the slurry which mixed said catalyst, a thickener, and distilled water, and was prepared to predetermined viscosity. It pulls up, after the honeycomb filter made from cordierite (for example, product made from NGK) is immersed for 10 minutes, After blowing off an excessive solution by a blowing air etc., after drying at 120 ** for 2 hours, calcinate in a 5-hour oxidizing atmosphere at 800 more **, and also said honeycomb filter is calcinated at 450 ** among the oxidizing atmosphere containing a sulfur oxide and a steam, The exhaust gas filter which coated the surface of said honeycomb filter with the carrier which supported the catalyst was obtained.

[0061]The activity evaluation test of the catalyst for exhaust gas purification in the <activity evaluation of catalyst> examples 1-9 and the comparative examples 1-9 was done. Drawing 2 is a schematic diagram of the fixed-bed flow system reaction apparatus used for the catalytic activity evaluation test. After the nitrogen gas 41 containing 100 ppm of sulfur oxides, the dry air 42, and SOF43 were adjusted by each of the flow preparation machines 44 and 45 for gases, and the flow preparation machines 46 for fluids in drawing 2 at the predetermined flow, It is mixed with the nitrogen gas 41 and the dry air 42 containing 100 ppm of sulfur oxides while SOF43 is evaporated with prescribed concentration in the vaporizer 47. This mixed gas is introduced in the quartz tube 48, and is purified by the catalyst 49 for exhaust gas purification placed into the quartz tube 48. The silica wool 50 is arranged before and behind the catalyst 49 for exhaust gas purification, and the quartz tube 48 is installed in the electric furnace 51. After introducing the purified mixed gas into the carbon monoxide of a NDIR method, and the choke-damp analyzer 52 and detecting carbon monoxide concentration and carbon dioxide levels, it is introduced into the oxygen sensor 53 and an oxygen density is measured. The catalytic activity evaluation test measured aging of catalytic activity on with 12% of the oxygen tension of mixed gas, the space velocity 30000/h-1, the SOF concentration of 300 ppm, the sulfur oxide gas concentration of 100 ppm, and a degree of electric furnace internal temperature of 250 ** conditions. The burning rate was computed by (several 1) from the carbon monoxide concentration and carbon dioxide levels which were measured by the above method.

[0062]

[Equation 1]

$$\text{SOF燃焼率（%）} = \frac{PCO + PCO_2}{PC} \times 100$$

[0063]The value of the carbon monoxide concentration by which PCO was measured with the carbon monoxide of a NDIR method, and a choke-damp analyzer in (several 1), PCO2 are the carbon monoxide of a NDIR method, and a value of the carbon dioxide levels measured by the choke-damp analyzer, and PC is the concentration of CO [on theory when SOF burns 100%], or CO2. Aging of the burning rate was shown in drawing 3 and drawing 4.

[0064]Drawing 3 is a figure showing aging of the burning rate of the catalytic activity evaluation test of the catalyst for exhaust gas purification in Examples 1-9, and drawing 4 is a figure showing aging of the burning rate of the catalytic activity evaluation test of the catalyst for exhaust gas purification in the comparative examples 1-9. The burning rate and horizontal axis in which the vertical axis was computed from (several 1) show accumulated time when it measures by the above-mentioned experimental condition among the figure.

[0065]In drawing 3 and drawing 4, Examples 1-3 and the comparative examples 1-3, It is a result at the time of calcinating in the oxidizing atmosphere which performs oxidizing atmosphere calcination for the case where oxidizing atmosphere calcination is performed, after reducing atmosphere calcination about Examples 4-9 and the comparative examples 4-9, and subsequently contains sulfur oxide gas further after

reducing atmosphere calcination. In any case, initial activity is high so that clearly from this drawing 3 and drawing 4. In the case of Examples 1-3, activity is falling a little with aging, but it is about 10%, and about Examples 4-9, the fall of activity is hardly seen, but the grade of a fall is high activity, and it turns out that it is long lasting. When the result of the comparative example shown in drawing 4 is looked at, on the other hand, the comparative examples 1-3, Although initial activity is comparatively high, the comparative examples 4-9 are low about 20% compared with the initial activity of the result shown in the example, and if the activity after aging is looked at, after 200-hour progress, any burning rate of a comparative example will fall till around 40%.
In low activity, it turns out that it is a short life.

[0066]As mentioned above, according to this example, as shown in Examples 1-3, in a mixing process, it turns out that it is long lasting with high activity compared with the former, and excels in endurance also only by adding the ligand which forms a catalytic activity ingredient and a complex although the fall of activity is seen a little. By calcinating by an oxidizing atmosphere and also calcinating in the oxidizing atmosphere containing sulfur oxide gas, after calcinating by reducing atmosphere also in a baking process, as shown in Examples 4-9, It turns out that the catalyst for exhaust gas purification which has a long life in high activity far compared with a conventional example is acquired.
[0067]Or decline in a burning rate was small compared with the catalyst for exhaust gas purification in a comparative example also about the catalyst for exhaust gas purification in which example of this invention, it is changeless and it turned out that it excels in the poisoning-proof nature by a sulfur oxide.
[0068]Next, the embodiment about the filter for exhaust gas purification which uses the catalyst for exhaust gas purification acquired by the manufacturing method of the catalyst for exhaust gas purification of this invention, the device for exhaust gas purification, and the system for exhaust gas purification is shown.
[0069](Embodiment 2) Drawing 5 is a sectional view of the catalyst filter for exhaust gas purification in Embodiment 2 which uses the catalyst which carried out ****** production for the manufacturing method of the catalyst for exhaust gas purification of this invention. In drawing 5, the heat-resistant honeycomb structure thing 5 catches the detrimental constituent in exhaust gas, The porous inorganic substance 6 supported by the surface of the heat-resistant honeycomb structure thing 5 provides the heat-resistant honeycomb structure thing 5 with high specific surface area, and the catalytic activity ingredient 7 supported by the upper surface of the porous inorganic substance 6 purifies the carbon monoxide in exhaust gas, hydrocarbon, and a particulate by oxidation combustion. The arrow of drawing 2 shows an inflow and outflow direction of exhaust gas.
[0070](Embodiment 3) Drawing 6 is a sectional view of the exhaust gas purifying facility in the embodiment of the invention 3. In drawing 6, from the exhaust-gas-flow entrance 9 formed in the case 8, carbon monoxide, Hydrocarbon and the exhaust gas containing a particulate flow in the case 8, the exhaust gas which flowed is purified by the catalyst 10 for exhaust gas purification stored by the case 8, and the purified exhaust gas is emitted from the exhaust emission outlet port 11 formed in the case 8.
[0071](Embodiment 4) Drawing 7 is a sectional view of the exhaust gas purifying facility in the embodiment of the invention 4. In drawing 7, from the exhaust-gas-flow entrance 13 formed in the case 12, carbon monoxide, Hydrocarbon and the exhaust gas containing a particulate flow in the case 12, The exhaust gas which the catalyst 14 for exhaust gas purification stored by the case 12 was heated by the heating method 16, and flowed according to the heated catalyst 14 for exhaust gas purification is purified, and the purified exhaust gas is emitted from the exhaust emission outlet port 15 formed in the case 12.
[0072](Embodiment 5) Drawing 8 is a sectional view of the exhaust gas purifying facility in the embodiment of the invention 5. In drawing 8, the exhaust gas which contains carbon monoxide, hydrocarbon, and a particulate by the blowing means 17 is accelerated, The accelerated exhaust gas flows in the case 18 from the exhaust-gas-flow entrance 19 formed in the case 18, The exhaust gas which flowed is heated by the heating method 20 provided in the case 18, the heated exhaust gas is purified by the catalyst 21 for exhaust gas purification stored in the case 18, and the purified exhaust gas is emitted from the exhaust emission outlet port 22 formed in the case 18.
[0073](Embodiment 6) Drawing 9 is a sectional view of the exhaust gas purifying facility in the embodiment of the invention 6. In drawing 9, 23 is an engine and a manifold part directly under an engine in 24, The exhaust gas containing the carbon monoxide, hydrocarbon, and the particulate which were exhausted from the engine 23 is accelerated by the blowing means 25, The accelerated exhaust gas flows in the case 26 from the exhaust-gas-flow entrance 27 formed in the case 26, The exhaust gas which flowed is heated by the heating method 28 provided in the case 26, the heated exhaust gas is purified by the catalyst 29 for

exhaust gas purification stored in the case 26, and the purified exhaust gas is emitted from the exhaust emission outlet port 30 formed in the case 26. In this Embodiment 6, a system without the heating method 28 or the heating method 28, and the blowing means 25 is also possible.

[0074](Embodiment 7) Drawing 10 is a sectional view of the exhaust gas purifying facility in the embodiment of the invention 7. In drawing 10, 31 is an engine and a manifold part directly under an engine in 32, Carbon monoxide, hydrocarbon, and the exhaust gas containing a particulate are introduced into the communication trunk 34 kept warm by the thermal insulation 33 from the engine 31, The introduced exhaust gas is accelerated by the blowing means 35 within the communication trunk 34, The accelerated exhaust gas flows in the case 36 from the exhaust-gas-flow entrance 37 formed in the case 36, The exhaust gas which flowed is heated by the heating method 38 provided in the case 36, the heated exhaust gas is purified by the catalyst 39 for exhaust gas purification stored in the case 36, and the purified exhaust gas is emitted from the exhaust emission outlet port 40 formed in the case 36. In this embodiment, a system without the heating method 38 or the heating method 38, and the blowing means 35 is also possible.

[0075]

[Effect of the Invention]As mentioned above, according to the exhaust gas filter, the exhaust gas purifying facility, and the system for exhaust gas purification using the catalyst for exhaust gas purification and this which carried out ******** production at the manufacturing method of the catalyst for exhaust gas purification of this invention, the following outstanding effects are acquired.

[0076]According to the invention according to claim 1, atomization and high decentralization of a catalytic activity ingredient are attained, and the catalyst for exhaust gas purification which the surface area of the catalyst which contributes to a reaction can enlarge remarkable, and has high activity can be acquired. The catalyst for exhaust gas purification which can process exhaust gas by a high purifying rate for a long period of time can be acquired by preventing poisoning of the catalytic activity ingredient by the sulfur oxide in exhaust gas. By using the catalyst for exhaust gas purification with which the fall of the catalyst function by poisoning was prevented, the catalyst for exhaust gas purification excellent in a catalyst function, endurance, and reliability can be acquired. The manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect to say is realizable.

[0077]According to the invention according to claim 2, in addition to the effect in claim 1, by configurating with a sulfur atom for a catalytic activity ingredient, From the atomic radius of the sulfur which forms the metal complex where physical properties were stabilized more, and serves as a ligand being larger than the atomic radius of the ligand of other complexing agents. A more nearly three-dimensional metal complex can be formed, as a result, the distance between metal ions becomes uniform in three dimensions, and the catalyst for exhaust gas purification which the dispersibility of the catalytic activity ingredient in a carrier surface uniformed can be acquired. The manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect to say is realizable.

[0078]According to the invention according to claim 3, it adds to claim 1 or the effect in 2, A catalytic activity ingredient forms two sulfur atoms and complexes which are contained in the salt of a diethyldithiocarbamic acid derivative, Under the present circumstances, the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect of being supported by high distribution with a fixed distance which exists when a sulphuric atomic radius forms a three-dimensional complex from a large thing and is supported by the carrier surface is realizable.

[0079]According to the invention according to claim 4, add to the effect in claim 3 and two sulfur atoms and complexes which are contained in diethyl diethyldithiocarbamate ammonium are formed, Under the present circumstances, while supporting to high distribution with a fixed distance which exists when a sulphuric atomic radius forms a three-dimensional complex from a large thing and is supported by the carrier surface, The manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that the complex stable with two diethyl ammonium is formed is realizable.

[0080]according to the invention according to claim 5 -- claims 1 thru/or 4 -- inner -- in addition to the effect in any 1, since a metal complex is formed efficiently, the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that the catalyst for exhaust gas purification of high activity can be acquired by low cost is realizable.

[0081]According to the invention according to claim 6, it adds to the effect of [1 / any] the claims 1 thru/or 5, The solubility of metal salt of a catalytic activity ingredient improves, complexing of a complexing agent becomes easy, the uniform dispersibility of a catalytic activity ingredient when it is considered as a catalyst improves, and the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that high activity of the catalyst for exhaust gas purification can be planned can be

realized.
[0082]According to the invention according to claim 7, in addition to the effect in claim 6, the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that the poisoning by chlorine can be controlled is realizable.
[0083]according to the invention according to claim 8 -- claims 1 thru/or 7 -- inner -- in addition to the effect in any 1, the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that the heat resistance of the catalyst for exhaust gas purification can be raised remarkably is realizable.
[0084]According to the invention according to claim 9, in addition to the effect in claim 8, the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect of changing an inertness ingredient to the oxidation reaction of the catalytic activity ingredients at an ingredient [activity / oxidation reaction] is realizable.
[0085]In addition to claim 8 or the effect in 9, when the counter ion of the salt of a catalyst component supports a catalyst, it remains, according to the invention according to claim 10, poisoning of the catalytic activity ingredient may be carried out by this, but. Since the steam was added, this remains ingredient can be removed and the activity of a catalytic activity ingredient can be raised, The manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect of changing at a thing [activity / oxidation reaction] what was inertness to the oxidation reaction of the catalytic activity ingredients is realizable.
[0086]According to the invention according to claim 11, it adds to the effect of [1 / any] the claims 8 thru/or 10, An ingredient [inertness / oxidation reaction / among catalytic activity ingredients] is changed to an ingredient [activity / oxidation reaction], and the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that high catalytic activity can be acquired can be realized.
[0087]According to the invention according to claim 12, it adds to the effect of [1 / any] the claims 8 thru/or 11, An ingredient [inertness / oxidation reaction / among catalytic activity ingredients] is changed to an ingredient [activity / oxidation reaction], and the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that high catalytic activity can be acquired can be realized.
[0088]According to the invention according to claim 13, it adds to the effect of [1 / any] the claims 1 thru/or 12, Also when heat-treating in the oxidizing atmosphere containing sulfur oxide gas, the reaction of a carrier and a sulfur oxide is inhibited, the fall of the specific surface area accompanying processing can be prevented, and the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that high catalytic activity can be attained can be realized.
[0089]According to the invention according to claim 14, the manufacturing method of the catalyst for exhaust gas purification which has the outstanding effect that in addition to the effect in claim 13 a catalytic activity ingredient is distributed and it can support with the state where it microatomized is realizable.
[0090]Since the carrier which distributed uniformly the catalytic activity ingredient excellent in poisoning-proof nature is supported to the cell wall according to the invention according to claim 15, while it can be efficient, being able to decompose and being able to purify SOF in exhaust gas, etc., it excels in endurance and the exhaust gas filter which raised reliability can be realized.
[0091]According to the invention according to claim 16, by preventing poisoning of the catalytic activity ingredient by the sulfur oxide in exhaust gas, While low-temperature exhaust gas as well as hot exhaust gas is efficient and being able to purify it by heating the catalyst for exhaust gas purification which can process exhaust gas by a high purifying rate for a long period of time, the exhaust gas purifying facility excellent in a high catalyst function and endurance, and reliability is realizable.
[0092]According to the invention according to claim 17, the exhaust gas purifying facility which can be easily attached to the exhaust system of a diesel power plant is realizable by in addition to the effect in claim 16, having stored the exhaust gas filter in the case and having established the inflow and the tap hole of exhaust gas in the case.
[0093]By according to the invention according to claim 18, in addition to the effect in claim 17, using the exhaust gas of the low temperature in the exhaust system of a diesel power plant as heating fluid, and spraying the catalyst for exhaust gas purification, The exhaust gas purifying facility which can also raise the purification efficiency of the exhaust gas in low temperature is realizable.
[0094]Since the exhaust gas purifying facility with the catalyst for exhaust gas purification with which the fall of the catalyst function by poisoning was prevented is used according to the invention according to

claim 19, While excelling in a catalyst function and excelling in endurance or reliability, the exhaust gas cleaning system which raised the purification efficiency of exhaust gas is realizable by controlling the temperature fall of exhaust gas.

[0095]According to the invention according to claim 20, in addition to the effect in claim 19, the exhaust gas cleaning system which raised the purification efficiency of exhaust gas is realizable by preventing the temperature fall of exhaust gas.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]Process drawing of the manufacturing method of the catalyst for exhaust gas purification in the embodiment of the invention 1
[Drawing 2]The schematic diagram of the fixed-bed flow system reaction apparatus used for the catalytic activity evaluation test
[Drawing 3]The figure showing aging of the burning rate of the catalytic activity evaluation test of the catalyst for exhaust gas purification in Examples 1-9
[Drawing 4]The figure showing aging of the burning rate of the catalytic activity evaluation test of the catalyst for exhaust gas purification in the comparative examples 1-9
[Drawing 5]This invention is a sectional view of the catalyst filter for exhaust gas purification in Embodiment 2.
[Drawing 6]The sectional view of the exhaust gas purifying facility in the embodiment of the invention 3
[Drawing 7]The sectional view of the exhaust gas purifying facility in the embodiment of the invention 4
[Drawing 8]The sectional view of the exhaust gas purifying facility in the embodiment of the invention 5
[Drawing 9]The sectional view of the exhaust gas purifying facility in the embodiment of the invention 6
[Drawing 10]The sectional view of the exhaust gas purifying facility in the embodiment of the invention 7
[Description of Notations]
1 Weighing process
2 Impregnation process
3 Drying process
4 Baking process
5 Heat-resistant honeycomb structure thing
6 A porous inorganic substance
7 Catalytic activity ingredient
8 Case
9 Exhaust-gas-flow entrance
10 The catalyst for exhaust gas purification
11 Exhaust emission outlet port
12 Case
13 Exhaust-gas-flow entrance
14 The catalyst for exhaust gas purification
15 Exhaust emission outlet port
16 Heating method
17 Blowing means
18 Case
19 Exhaust-gas-flow entrance
20 Heating method
21 The catalyst for exhaust gas purification
22 Exhaust emission outlet port
23 Engine
24 Manifold part
25 Blowing means
26 Case
27 Exhaust-gas-flow entrance

28 Heating method
29 The catalyst for exhaust gas purification
30 Exhaust emission outlet port
31 Engine
32 Manifold part
33 Thermal insulation
34 Communication trunk
35 Blowing means
36 Case
37 Exhaust-gas-flow entrance
38 Heating method
39 The catalyst for exhaust gas purification
40 Exhaust emission outlet port
41 Nitrogen gas
42 Dry air
43 SOF
44 The flow regulator for gases
45 The flow regulator for gases
46 The flow regulator for fluids
47 Vaporizer
48 Quartz tube
49 The catalyst for exhaust gas purification
50 Silica wool
51 Electric furnace
52 The carbon monoxide of a NDIR method, a choke-damp analyzer
53 Oxygen sensor

[Translation done.]